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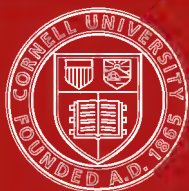
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REPORT ON RADIATION
AND THE
QUANTUM-THEORY.

BY
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PRINCIPAL REFERENCES OTHER THAN THE DETAILED PAPERS REFERRED TO IN THE TEXT.

“*La Theorie du Rayonnement et les Quanta.*” (Gauthier-Villars, Paris, 1912.) Reports presented to the first Solway Congress of Physics at Brussels (October, 1911), with the discussion thereon.

[Reports presented by Lorentz, Jeans, Warburg, Rubens, Planck, Knudsen, Perrin, Nernst, Kamerlingh-Onnes, Sommerfeld, Langevin and Einstein, nearly all dealing with the Quantum-Theory. Comments and discussion by the foregoing, and also by Poincaré, Lord Rayleigh, Wien, Rutherford, Brillouin, Mme. Curie, Hasenöhl, De Broglie and Lindemann.]

“*Vorträge über die Kinetische Theorie der Materie und der Elektrizität*”; *Mathematische Vorlesungen an der Universität Göttingen.* (Teubner, Leipzig, 1914.)

[Reports by Planck, Debye, Nernst, v. Smoluchowski, Sommerfeld, Lorentz and others, largely concerned with the developments of the Quantum-Theory.]

“*Report of the British Association (1913) at Birmingham.*” Section A.—Discussion on Radiation; pp. 376-386.

[Discussion by Lorentz, Pringsheim, Love and Larmor. Opening by Jeans.]

Max Planck: “*Acht Vorlesungen über Theoretische Physik.*” (S. Hirzel, Leipzig, 1910.)

[The fifth and sixth lectures deal with Planck’s form of the Quantum-Theory.]

Henri Poincaré: “*Dernières pensées.*” (Flammarion, Paris, 1913.) [An essay, entitled “*L’hypothèse des Quanta,*” gives in a non-technical form Poincaré’s final judgment on the Quantum-Theory.]

RADIATION AND THE QUANTUM-THEORY.

CHAPTER I.

ON THE NEED FOR A QUANTUM-THEORY.

Introductory.

1. The quantum-theory, which is now found to be applicable in many departments of physical science, had its origin in an attempt to account for the spectrum of black-body radiation. It is therefore appropriate, as well as convenient, that the present report should approach the theory through the radiation problem. The arrangement adopted will be as follows: We shall first explain how the quantum-theory is demanded, and indeed made inevitable, by the known facts of black-body radiation (Chapters I. and II.); we shall next discuss the radiation problem with the help of the quantum-theory (Chapter III.), and shall then proceed to consider the bearing of the quantum-theory on certain other problems of physics, namely, the line spectra of the elements (Chapter IV.), the photo-electric effect (Chapter V.), and the specific heats of solids (Chapter VI.) A final chapter is devoted to discussing whether a physical basis can be found for the conceptions of the theory.

2. The quantum-theory, it will be understood from the outset, represents a complete departure from the old Newtonian system of mechanics. Until the end of the last century, the Newtonian mechanics had shown a capacity of explaining and interpreting practically all the phenomena to which it had been applied. It was natural that physical science should attempt to progress by explaining more and more phenomena in terms of the Newtonian mechanics. It was hoped that whatever phenomena still defied explanation would, with the acquisition of more intimate knowledge, be ultimately found to be simply further illustrations of the truth of the Newtonian system of laws.

Gradually certain phenomena have emerged from the general

mass as resisting explanation in terms of these laws, and the conviction has more and more developed that something outside the Newtonian laws is needed for their explanation. Of course, the mere discovery that a phenomenon is difficult to explain in the Newtonian way is no adequate reason for abandoning a system of laws which is known to hold throughout vast regions of natural phenomena; what we have to discuss is whether there are not certain phenomena which are in flat contradiction to the Newtonian laws. From demonstrating that a matter is difficult to proving that it is impossible is a long step, but if this step can be taken with respect to the explanation of even one well-established phenomenon of Nature, then the logical necessity of rejecting the impossibility becomes unanswerable.

The phenomenon which is believed to provide the crucial test as to the universal validity of the Newtonian mechanics is the following: *the total radiant energy per unit volume of ether in temperature-equilibrium with matter is finite, and not infinite.* It is a matter merely of mathematical demonstration that this fact is incompatible with Newtonian mechanics. Of course, it cannot be denied that the phenomenon itself is in some ways open to question. It may be argued that there are at least the possibilities that radiation never can be in temperature-equilibrium with matter, or that ether as a seat of energy is a figment of the imagination. These possibilities must, of course, be discussed. It may be argued that the mathematical proof is open to question: the proof in its finished form was given by Poincaré, and the validity of his mathematical reasoning has never been challenged, but this cannot carry absolute conviction. Like every other scientific judgment the matter has to be one of balancing probabilities. But a search for the considerations to be put in the other side of the balance reveals, to many minds at least, a total deficiency of real logical arguments. We, as physical machines, are built on a scale which is large compared with the scale of light waves and electrons, from which it has resulted that our first physical experiments, as a race, have been concerned with matter also on a scale very large in comparison with its ultimate structure. The Newtonian laws have undoubtedly been found adequate to explain the whole series of what we may call large-scale phenomena, but no adequate reasons have, so far, been given for asserting that they must also be the laws which govern small-scale phenomena. The fact seems to be that the old laws are not,

so to speak, fine-grained enough to supply the whole truth with regard to small-scale phenomena.

In view of the fact that our preconceived ideas must necessarily form the starting point in every train of thought, and that these preconceived ideas are very intimately bound up with the Newtonian mechanics, it seems advisable to begin the present report with an explanation of the reasons which are believed to compel the abandonment of this system. In the present chapter these reasons are discussed in a purely physical way, without mathematical analysis and therefore, of course, without rigorous proof. In Chapters II. and III., which are largely mathematical, an account is given of the analysis which is needed to work out the physical ideas discussed in the first chapter. The report is so arranged that the mathematical parts of Chapters II. and III. may conveniently be omitted by those readers whose interest centres mainly in physical ideas rather than in abstract reasoning. The contents of the subsequent chapters have been already explained and are sufficiently indicated by their titles.

The Crucial Phenomenon.

3. As has already been stated the phenomenon which it is convenient to consider first, as providing a crucial test of the Newtonian mechanics, is the phenomenon that *the total radiant energy per unit volume of ether in temperature-equilibrium with matter is finite, and not infinite.*

Assuming for the moment the truth of this as an experimental fact, we may try to understand its physical bearings. To make the question as definite and as simple as possible, let us fix our attention on an enclosure with perfectly reflecting walls in which there is a mass of, say, iron at $0^{\circ}\text{C}.$, and let us suppose that there is a state of equilibrium inside this enclosure. The iron is continually radiating energy out from its surface into the surrounding ether inside the enclosure; and is also absorbing energy from the ether. From the condition of equilibrium, the rates of exchange must just balance. If we assume, for additional simplicity, that the iron is coated with a perfectly absorbing paint, then in point of fact each square centimetre of surface emits 3×10^5 ergs of radiation per second into the ether, and also absorbs 3×10^5 ergs per second of radiation falling on to it from the ether. The energy in the ether is of density 4×10^{-5} ergs per cubic centimetre; the heat energy in the iron is of the order of 8×10^9 ergs per cubic centi-

metre. The heat energy of the iron resides in the oscillations of its atoms, each atom moving with an average velocity of about 30,000 cms. per second.

4. A very little consideration will show that this state of things is different from what might be expected by analogy from other systems which are known to obey the ordinary dynamical laws. Consider, for instance, a tank of water (to represent the ether) in which is floated a system of corks (to represent atoms of matter) connected by light springs or elastics so that they can oscillate relatively to one another. Suppose that initially the surface of the water is at rest. Let the system of corks be set into violent oscillation and placed on the surface of the water. The motion of the corks will set up waves in the water, and these waves will spread all over the surface of the water, undergoing reflection when they meet the walls of the tank. We know that ultimately the corks will be reduced to rest; the energy of their motion will be transformed first into the energy of waves and ripples on the surface of the water, and then, owing to the viscosity of the water, into heat energy in the water. A final state in which the corks continue to oscillate with extreme vigour while the water has almost no energy is unthinkable; we expect a final state in which practically all the energy has found its way into the water.

5. Let us examine another analogy. Let the corks be replaced by spherical lead shot, again connected by light springs, and let the system be suspended in a closed chamber containing air. After the system of shot has been started in violent oscillation, let the chamber be closed up. The motion of the shot will set up waves in the air, and these will again be dissipated by viscosity. A final steady state in which the spheres continue to oscillate with high velocities for ever is again unthinkable. In point of fact, we know that the final state will be one in which the spheres are all at rest in their positions of equilibrium, or rather, to be quite precise, in which they oscillate with the infinitesimally small velocities of the Brownian movements appropriate to particles of their size; practically all the energy will have passed from the spheres into the surrounding air.

The Kinetic Theory of Gases enables us to trace out the transformation of the energy which originally resided in the oscillations of the spheres. In the final steady state we know that this energy will be the heat energy of the air. Let us

simplify the discussion by assuming that the air was originally at or close to the absolute zero of temperature, and suppose that in the steady state the temperature of the air is T . If there are N molecules of air, their energy in the steady state will be $\frac{5}{2} NRT$, and if there are n spheres, the energy of their Brownian movements will be $\frac{3}{2} nRT$, where R is the gas constant. The total energy in the steady state will be $\left(\frac{5}{2}N + \frac{3}{2}n\right)RT$, and T will be determined from the condition that this quantity must be equal to the total energy of the original oscillations of the spheres. Since N , the number of molecules, will be enormously large compared with n , the number of spheres, it is clear that practically all the energy will be contributed by the term $\frac{5}{2}NRT$. By the time the steady state is reached the energy is almost entirely transferred from the spheres to the gas.

The molecules of the gas move with velocities determined statistically by the well-known law of Maxwell. Suppose that the position and velocity of every molecule were known at any instant, then, by an application of Fourier analysis, it would be possible to regard this motion as made up of trains of waves—i.e., any molecular motion, however complex, can be regarded as coinciding at each instant with the motion produced by a certain system of sound waves in the air, and the energy of the molecular motion will be exactly the same as the energy of these trains of waves (*cf.* Chapter VI. below). If the molecular velocities at any instant obey Maxwell's law, it is found* that the energy of these trains of waves is distributed between the different wave-lengths according to the law

$$4\pi RT \lambda^{-4} d\lambda. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

That is to say, if we could devise some system of resonators which would pick up and sort out the molecular motions in the way in which a spectroscope sorts out light, then the energy per unit volume of the waves of wave-length intermediate between λ and $\lambda + d\lambda$ would be found to be that expressed in formula (1). One reservation has to be made with respect to this formula, namely, that it does not apply to waves of wave-length as short as, or comparable with, the distance

* *Cf.* "Temperature-radiation and the Partition of Energy in Continuous Media," *Phil. Mag.* 17, p. 229 (Feb., 1909).

between adjacent molecules. But a good approximation can be obtained by supposing that the formula holds accurately from $\lambda = \infty$ to a limiting wave-length λ_m , and that there are no waves at all of wave-length shorter than λ_m . The total energy is then

$$\int_{\lambda=\infty}^{\lambda=\lambda_m} 4\pi RT \lambda^{-4} d\lambda = \frac{4}{3} \frac{RT}{\lambda_m^3}, \quad . \quad . \quad . \quad . \quad (2)$$

and λ_m can be found by equating this to the total energy of the molecules.

Of the energy under consideration, analysed by the integral in equation (2), it will be seen that only one-eighth of the total energy will be of wave-length greater than $2\lambda_m$, while seven-eighths is of wave-length intermediate between this and λ_m . In a chamber filled with ordinary air λ_m will be of the order of 10^{-7} cms. Only one millionth part of the total energy will be of wave length greater than 10^{-5} cms. Thus we may say that the energy tends to run almost entirely into the shortest wave-lengths which are possible in the medium.

6. It is now possible to explain (a statement of the proof being reserved for the next chapter) why it is that the Newtonian mechanics are inadequate to account for the facts of radiation. For whatever is regarded as certain or uncertain about the ether, it must be granted as quite certain that it approaches more closely to a continuous medium than to a gas. If it has any grained structure at all the distance between adjacent grains must be enormously less than the 10^{-7} cms. assumed for the corresponding distance in the gas. But even if this distance were as great as 10^{-7} cms., only one-millionth of the total radiant energy ought to be of wave-length as great as 10^{-5} cms.—entirely contrary to what is observed. And if, as seems most probable, the ether is a perfectly grainless structure, then the quantity λ_m will be zero; the integral corresponding to integral (2) must be evaluated from $\lambda=0$ to $\lambda=\infty$, and the total energy will be infinite. This is why the crucial fact we have mentioned above is believed to decide against the Newtonian mechanics.

To put the matter shortly: in all known media there is a tendency for the energy of any systems moving in the medium to be transferred to the medium and ultimately to be found, when a steady state has been reached, in the shortest vibrations of which the medium is capable. This tendency can be shown (Chapter II.) to be a direct consequence of the Newtonian laws.

This tendency is not observed in the crucial phenomenon of radiation; the inference is that the radiation phenomenon is determined by laws other than the Newtonian laws.

A brief sketch of the line of proof used to establish the quantum-theory may appropriately be given here before the proof itself is given. The first step is not essential to the establishment of the quantum-theory, but is helpful as confirming the theory. It consists in examining the final state of a medium in which the motion is governed by the Newtonian laws. The tendency of the energy to run into the vibrations of shortest wave-length is found to admit of rigorous proof. The second step is the really essential one. It consists in working back from the observed final partition of energy in the ether to the laws by which this partition of energy must be produced. It can be shown that, if the final partition of energy is that given by the well-known law of Planck, then the motion of the medium must be governed by laws which involve the quantum-theory. Further, if Planck's law, instead of expressing the exact truth, expresses only an approximation to the truth, then the fundamental laws must be generally similar to those of the quantum-theory; at least they must be based on discontinuities, and not on the ideas of continuity involved in the classical mechanics.

CHAPTER II.

GENERAL DISCUSSION OF THE RADIATION PROBLEM, ACCORDING TO THE CLASSICAL MECHANICS.

7. The radiation which is in thermodynamical equilibrium with matter at temperature T is spoken of as "full radiation" or "black-body radiation" at temperature T . According to Stefan's law its total intensity is proportional to T^4 ; according to Wien's displacement law, its energy, distributed according to wave-length, is of the form

$$F(\lambda T) \lambda^{-5} d\lambda, \quad (3)$$

where F is a function, undetermined so far as Wien's law goes, of the product λT . From Wien's law, Stefan's law can be deduced at once on integrating from $\lambda=0$ to $\lambda=\infty$.

Both Stefan's law and Wien's law can be deduced from general thermodynamical considerations, but such considerations do not suffice to determine the actual form of the function F in Wien's law. Both of these laws can be tested experimentally, and they are found to be in agreement with observation. The form of the function F can be determined experimentally, and the form which has been found to agree most closely with experiment is that suggested by Planck in 1901 in a paper* which has since provided the basis for the quantum-theory. Planck's form, which is derived from considerations similar to those on which the quantum-theory now rests,† is

$$\lambda^{-5} F(\lambda T) = \frac{8\pi h \nu}{e^{h\nu/RT} - 1},$$

where ν is the frequency corresponding to wave-length λ , and h is the constant, now known as Planck's constant, of which the value is approximately

$$6.6 \times 10^{-27} \text{ (ergs} \times \text{sec.)}.$$

Substituting this form for $F(\lambda T)$ into expression (3), the

* "Annalen der Physik," 4 (1901), p. 553.

† Cf. below, Chapter VII., §§ 62, 63.

partition of full black-body radiation at temperature T is found to be

$$8\pi RT\lambda^{-4}d\lambda \frac{x}{e^x - 1}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where x stands for $h\nu/RT$. This formula is believed to agree extremely well with experiment.*

8. Any radiation formula corresponding to a steady state must be derived by expressing that the amount of energy gained by the ether is equal to the amount absorbed. If $\varphi(\lambda, T)d\lambda$ is the law of partition of energy according to wave-length, there must be an equation of the form

$$\frac{\partial \varphi}{\partial t} = E - A,$$

where E stands for the rate of emission and A for the rate of absorption; and the steady state is determined by the condition $\frac{\partial \varphi}{\partial t} = 0$, or $E = A$.

In general, it may be expected that several agencies will be at work in the processes of emission and absorption. Planck, in his theory already referred to, supposed that the emission and absorption were accomplished by "resonators" of perfectly definite periods. These cannot of course account for the whole of the emission and absorption; let the parts due to them be denoted by E_R , A_R . An agency which must contribute something to the emission and absorption is to be found in the motion of free electrons in the matter; let us denote their contributions by E_E , A_E . A further agency is probably the photo-electric effect; when an electron is discharged there is an absorption of radiation; when one recombines there will be an emission of radiation. Let the contributions of the photo-electric effect be denoted by E_P , A_P . Treating any other agencies in the same way, we shall have an equation of the form

$$\frac{\partial \varphi}{\partial t} = (E_R - A_R) + (E_E - A_E) + (E_P - A_P) + \dots$$

The absorptions A_R , A_E , $A_P \dots$ may each be expected to contain φ as a factor; if we double the radiant energy of any wave-length we expect twice as much to be absorbed. Let

* For a discussion see "La Théorie du Rayonnement et les Quanta" (Gauthier-Villars, 1912).

us then put $A_R = B_R\phi$, &c. In general, the emissions E_R, E_E, \dots will not depend on ϕ , but let us make the matter as general as possible by assuming that they each contain a term in ϕ . Let us then put $E_R = F_R + G_R\phi$, &c., in which any or all of the G 's may vanish. We then have

$$\frac{\partial \phi}{\partial t} = (F_R + G_R\phi - B_R\phi) + (F_E + G_E\phi - B_E\phi) + (F_P + G_P\phi - B_P\phi) + \dots$$

and the equation giving the steady state is

$$\phi = \frac{F_R + F_E + F_P + \dots}{(B_R - G_R) + (B_E - G_E) + (B_P - G_P) + \dots} \quad (5)$$

It is to be expected that the ratios of the different terms, both in the numerator and denominator, will vary from substance to substance. For instance, F_E and $B_E - G_E$ will be small for insulators or bad conductors in which there are few electrons, F_R and $B_R - G_R$ will be small for substances which possess few resonators of the frequency under consideration, and F_P and $B_P - G_P$ will be small for substances in which the photo-electric effect is slight at this frequency. On the other hand, observation shows that ϕ has precisely the same value for all substances. Now in order that ϕ may be the same for all substances, no matter what the relative values of F_R, F_E and F_P may be, it is necessary, as a matter of algebra, to have

$$\frac{F_R}{B_R - G_R} = \frac{F_E}{B_E - G_E} = \frac{F_P}{B_P - G_P} = \dots = \phi, \quad (6)$$

giving at once $E_R = A_R, E_E = A_E$ and $E_P = A_P$.

In other words, each agency in the mechanism of emission and absorption must, considered by itself, be capable of setting up the full black-body radiation, and must not set up any radiation different from this; if this were not so, the black-body radiation would vary from substance to substance.

Algebraically, it is of course conceivable that one agency might have so slight an influence that ϕ , as given by equation (5) might have a value indistinguishable from its true value, while the fraction corresponding to this agency in equation (6) might have a value widely different from ϕ . The numerator and denominator would simply have both to be very small. But physically this would be inconsistent with the second law of thermodynamics*; and, in fact, it would require that in the

* Cf. Poincaré, "Journ. de Phys.," 11 (1912), p. 34.

final steady state energy should continuously flow in a closed cycle through the different mechanisms in turn, a possibility which may be excluded from serious consideration.

We may now proceed to consider the radiation from these different agencies in turn, beginning with that from "resonators."

Radiation from Resonators.

9. Let a resonator be considered as a dynamical system, obeying the classical laws. Let its frequency be $p/2\pi$, and let its kinetic and potential energies T and V be supposed given by

$$T = \frac{1}{2}\beta\dot{\varphi}^2, \quad V = \frac{1}{2}\alpha\varphi^2,$$

where φ is the co-ordinate expressing the state of the resonator and α and β are constants such that $p^2 = \alpha/\beta$.

The equation of motion, expressing the change in φ , is

$$\beta\ddot{\varphi} + \alpha\varphi = \Phi, \quad (7)$$

where Φ is the generalised force acting to increase φ . On multiplying by $\dot{\varphi}$, we obtain

$$\frac{d}{dt}(T+V) = \Phi\dot{\varphi},$$

so that the energy gained by the resonator in the time from 0 to t is

$$\int_0^t \Phi\dot{\varphi} dt. \quad \dots \dots \dots (8)$$

The solution of equation (7) can be written down in the usual way.* Suppose that at time $t=0$, the values of φ and $\dot{\varphi}$ are the same as if the resonator were performing an oscillation specified by $\dot{\varphi} = A \cos (pt - \varepsilon)$. The impulse $\Phi_t dt$, acting through the small interval dt at time t' , produces a superimposed oscillation such that the value of $\dot{\varphi}$ initially is $\frac{1}{\beta}\Phi_t dt$, and, therefore, such that the subsequent value of $\dot{\varphi}$ is $\frac{1}{\beta}\Phi_{t'} \cos p(t-t')dt$. Hence the total value of $\dot{\varphi}$ after time t is

$$\dot{\varphi} = \frac{1}{\beta} \int_{t'=0}^{t'=t} \Phi_{t'} \cos p(t-t') dt + A \cos (pt - \varepsilon),$$

* Lord Rayleigh, "Theory of Sound," §66.

and the total absorption in time t , as given by expression (8), is

$$\int_0^t \Phi \dot{\varphi} dt = \frac{1}{\beta} \int_0^t \int_0^{t'} \Phi_{t'} \Phi_{t''} \cos p(t' - t'') dt' dt'' + \int_0^t A \cos (pt - \varepsilon) \Phi dt.$$

On summing over a great number of oscillations, the second term on the right may be neglected, and the equation written in the form

$$\int_0^t \Phi \dot{\varphi} dt = \frac{1}{2\beta} \int_0^t \int_0^t \Phi_{t'} \Phi_{t''} \cos p(t' - t'') dt' dt'', \quad . . . \quad (9)$$

the divisor 2 appearing because the integration is over a square in the $t't''$ plane, instead of over the half-square bounded by the line $t'' = t'$.

The value of Φ from time 0 to t can be expressed as a Fourier series in the form

$$\Phi = \frac{1}{\pi} \int_0^\infty (F_p \cos pt + G_p \sin pt) dp,$$

where the coefficients F_p , G_p are given by

$$F_p = \int_0^t \Phi_{t'} \cos pt' dt', \quad \quad (10)$$

$$G_p = \int_0^t \Phi_{t'} \sin pt' dt', \quad \quad (11)$$

and in terms of these coefficients equation (9) may clearly be expressed in the form

$$\int_0^t \Phi \dot{\varphi} dt = \frac{1}{2\beta} (F_p^2 + G_p^2). \quad \quad (12)$$

But from a theorem given by Lord Rayleigh,*

$$\int_0^t \Phi^2 dt = \frac{1}{\pi} \int_0^\infty (F_p^2 + G_p^2) dp,$$

so that the mean value of Φ^2 from 0 to t , say $\bar{\Phi}^2$, is given by

$$\bar{\Phi}^2 = \int_0^\infty f(p) dp,$$

where $f(p) = \frac{1}{\pi t} (F_p^2 + G_p^2)$, and the mean rate of absorption is, from equation (12),

$$\frac{1}{t} \int_0^t \Phi \dot{\varphi} dt = \frac{1}{2\beta t} (F_p^2 + G_p^2) = \frac{\pi}{2\beta} f(p).$$

* "Phil. Mag.," [5], 27, p. 466.

If the force Φ arises from an electric intensity X in any direction in the ether, we may assume $\Phi=cX$, where c is a constant. Assume the density of radiant energy in the ether, resolved into its constituent frequencies, to be $\int_0^\infty R(p)dp$ per unit volume, then the mean value of X^2 will be $\frac{4\pi}{3}\int_0^\infty R(p)dp$, and c^2 times this will be $\bar{\Phi}^2$, which is equal to $\int_0^\infty f(p)dp$. Thus,

$$f(p)=\frac{4\pi}{3}c^2R(p),$$

and the mean rate of absorption of radiant energy by the resonator is $\frac{\pi}{2\beta}f(p)$, or $\frac{2\pi^2c^2}{3\beta}R(p)$.

If the radiating mechanism is electrical, we may take the emission in time t to be given by either of the equivalent forms

$$\int_0^t C\ddot{\phi}^2 dt = - \int_0^t C\dot{\phi}\ddot{\phi} dt,$$

where C is a constant. (The left-hand member will give the expression of Larmor, the right-hand that of Lorentz.) On substituting for $\ddot{\phi}$ from equation (7), the emission in time t is

$$-\frac{C}{\beta}\int_0^t \dot{\phi}(\dot{\Phi}-\alpha\dot{\phi})dt.$$

On integrating (10) and (11) by parts

$$F_p = -\frac{1}{p}\int_0^t \dot{\Phi}_r \cos pt' dt'; \quad G_p = \frac{1}{p}\int_0^t \dot{\Phi}_r \sin pt' dt',$$

so that

$$\int_0^t \dot{\phi} \dot{\Phi} dt = \frac{p}{2\beta}(G_p F_p - F_p G_p) = 0,$$

and the emission in time t is

$$\frac{C}{\beta}\int_0^t \alpha \dot{\phi}^2 dt.$$

Thus the average rate of emission is

$$\frac{C}{\beta}\overline{\alpha \dot{\phi}^2} = \frac{C}{\beta}p^2\overline{\beta \dot{\phi}^2},$$

where a bar over any quantity denotes that its average value is to be taken over the interval of time from 0 to t .

On equating emission and absorption, the condition for a steady state is found to be

$$R(p) = \frac{3C}{2\pi^2 c^2} p^2 \overline{\beta \dot{\phi}^2},$$

so that, in the steady state, the partition of radiant energy in the ether must be

$$R(p)dp = \frac{3C}{2\pi^2 c^2} \overline{\beta \dot{\phi}^2} p^2 dp. \quad . \quad . \quad . \quad . \quad (13)$$

As soon as the nature of the resonator is definitely known, C and c will be known. For a Hertzian oscillator* $C/c^2 = \frac{2}{3V^3}$, where V is the velocity of light, so that

$$R(p)dp = \frac{\overline{\beta \dot{\phi}^2}}{\pi^2 V^3} p^2 dp. \quad . \quad . \quad . \quad . \quad (14)$$

If the resonator consists of a single electron capable of oscillating with frequency p , $C = \frac{2}{3} \frac{e^2}{V^3}$, $c = e$, so that $C/c^2 = \frac{2}{3V^3}$ as before, and formula (14) again gives the partition of energy in the ether.

Radiation from Free Electrons.

10. A free electron may to some extent be treated as a resonator of zero frequency in the sense that it is the limit of an oscillating electron when the forces acting on it are made to vanish. We can suppose the ϕ of the preceding analysis to be a co-ordinate x measured in any direction; the kinetic energy T of this motion is $\frac{1}{2} m \dot{x}^2 = \frac{1}{2} m u^2$, so that $\beta = m$. Again $C = \frac{2}{3} \frac{e^2}{V^3}$, $c = e$, so that formula (14) is true, but now only for the limit in which $p = 0$. The formula becomes

$$R(p)dp = \frac{\overline{m u^2}}{\pi^2 V^3} p^2 dp. \quad . \quad . \quad . \quad . \quad (15)$$

This only gives the limiting form of $R(p)$ when $p = 0$. We can find the general form in the following way.

* Planck gives a slightly different proof for the Hertzian oscillator, see "Acht Vorlesungen über Theoretische Physik," Lecture V., or "Ann. d. Physik," 4 (1901), p. 556.

A single ray of light propagated parallel to the axis of x will be specified by equations of the form

$$\begin{aligned} X=0, \quad Y=A \cos \kappa(x+Vt), \quad Z=0, \\ \alpha=0, \quad \beta=0, \quad \gamma=-A \cos \kappa(x+Vt). \end{aligned}$$

The motion of an electron moving in the field of force arising from this wave of light may be regarded as compounded of—*

(i.) A uniform velocity of translation of components u_0, v_0, w_0 —the undisturbed velocity of the electron.

(ii.) Oscillations parallel to the axes of x and y , each of a purely harmonic nature and of frequency κw , where $w=u_0+V$, this latter being, of course, obtained by modifying the frequency of the incident light in accordance with the Doppler principle.

According to the classical dynamics the electron will absorb light of frequency κV . The emitted light will be of different frequencies for different directions of emission; the frequency corresponding to any direction will be obtained by modifying the frequency κw of the oscillation in accordance with Doppler's principle.

Let the usual polar co-ordinates r, θ, φ be taken, the electron being the origin and the axis of x being $\theta=0$. In any direction θ, φ the component of velocity of the electron will be

$$u_0 \cos \theta + v_0 \sin \theta \cos \varphi + w_0 \sin \theta \sin \varphi,$$

so that the frequency p of the radiation emitted in this direction will be given by

$$p = \kappa w V / (V - u_0 \cos \theta - v_0 \sin \theta \cos \varphi - w_0 \sin \theta \sin \varphi). \quad (16)$$

Let the distribution of intensity of radiation in different directions be supposed given by the formula $I(\theta, \varphi) \sin \theta d\theta d\varphi$; let the mean value of $u_0^2 + v_0^2 + w_0^2$ averaged over a great length of time be c^2 , and let the proportion of the whole time in which the velocity components lie within a small range

$$du_0, dv_0, dw_0 \text{ be } Af\left(\frac{u_0^2 + v_0^2 + w_0^2}{c^2}\right) du_0 dv_0 dw_0.$$

* A more rigorous proof and discussion will be found in a Paper in "Phil Mag.," Jan., 1914, p. 14.

Then the average total radiation emitted by the electron per unit time will be

$$\iiint \iiint Af\left(\frac{u_0^2 + v_0^2 + w_0^2}{c^2}\right) I(\theta, \varphi) \sin \theta d\theta d\varphi du_0 dv_0 dw_0,$$

where the integration is over all values of u_0, v_0, w_0, θ and φ , and the frequency of any particular element is given by equation (16).

This radiation can be analysed into its different frequencies by changing the variables from u_0, v_0, w_0, θ and φ to $u_0, w_0, \theta, \varphi$ and p by the help of equation (16) and then integrating with respect to u_0, w_0, θ and φ . The final result is found to be of the form*

$$\int \frac{1}{p_0} \Phi\left(\frac{p}{p_0}, c^2\right) dp, \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where p_0 stands for κV , 2π times the frequency of the incident light, and Φ is a function of which the particular form does not matter for the present purpose.

Clearly if the electron is acted on by a number of waves traversing the ether simultaneously the resulting emission of radiation will be the sum of a number of integrals, each of the type of (17).

Now, suppose that the electron is in a region of space in which the law of partition of radiant energy is $R(p_0)dp_0$, this energy being distributed at random as regards direction. Suppose that a unit amount of energy of frequency p_0 is, as the result of interaction with the free electron, replaced by an amount of energy ψ of the original frequency p_0 , and a spectrum $fF(p_0, p)dp$ of scattered energy. From formula (17), $F(p_0, p)$ must be of the form

$$F(p_0, p) = \frac{1}{p_0} \Phi\left(\frac{p}{p_0}, c^2\right),$$

and from the conservation of energy we must have

$$1 - \psi = \int_0^\infty F(p_0, p) dp = \int_0^\infty \Phi\left(\frac{p}{p_0}, c^2\right) \frac{dp}{p_0}. \quad . \quad . \quad (18)$$

Clearly on integration this last is a function of c^2 only, so that ψ is independent of p_0 .

* For details, see the Paper already referred to.

After unit time the law of partition of the whole amount of radiation will be

$$\psi \int R(p_0) dp_0 + \int dp \int_0^\infty R(p_0) F(p_0, p) dp,$$

or, arranged according to frequency p ,

$$\int [\psi R(p) + \int_0^\infty R(p_0) F(p_0, p) dp_0] dp. \quad . \quad . \quad (19)$$

The condition that the system shall have reached a final steady state is that the partition of radiant energy shall be unaltered by the interaction with the electron. The final partition of energy (19) must accordingly be identical with the initial partition of energy $\int R(p) dp$, and so we must have

$$\psi R(p) + \int_0^\infty R(p_0) F(p_0, p) dp_0 = R(p)$$

$$\text{or} \quad R(p)(1-\psi) = \int_0^\infty R(p_0) \Phi\left(\frac{p}{p_0}, c^2\right) \frac{dp_0}{p_0}.$$

The solution of this integral equation will give the form assumed by $R(p)$ in the steady state. If we put $p_0 = \chi p$, the equation becomes

$$\int_{\chi=0}^{\chi=\infty} \frac{R(\chi p)}{R(p)} \Phi\left(\frac{1}{\chi}, c^2\right) \frac{d\chi}{\chi} = 1 - \psi,$$

so that $R(\chi p)/R(p)$ must be independent of p . It follows that $R(p)$ must be of the form $R(p) = Bp^n$, where B and n are constants, so that the partition of energy in the ether must be given by

$$R(p) dp = Bp^n dp.$$

The values of the constants B and n can at once be found by comparison with formula (15), which gives the limiting form of $R(p)$ when $p=0$. Clearly we must have $n=2$ and $B = \frac{mu^2}{\pi^2 V^3}$. Thus the general value of $R(p)$ must be given by

$$R(p) dp = \frac{mu^2}{\pi^2 V^3} p^2 dp. \quad . \quad . \quad . \quad . \quad (20)$$

Thus the result obtained from the classical dynamics is that if $R(p)$ has this form there can be permanent equilibrium between the free electrons and radiation, but if $R(p)$ has any

other form, there will be a continued adjustment and exchange of energy until $R(p)$ has assumed this form.

11. According to the kinetic theory of matter, the mean value of $\overline{mu^2}$ for an electron, which has been denoted by $\overline{mu^2}$, ought to be equal to RT , where R is the gas constant and T the absolute temperature of the matter. Richardson and Brown* have determined the value of $\overline{mu^2}$ by direct experiment, and find that it is in point of fact exactly equal to RT . If we substitute this value for $\overline{mu^2}$, formula (20) becomes

$$R(p)dp = \frac{RT}{\pi^2 V_3} p^2 dp. \quad . \quad . \quad . \quad . \quad (21)$$

Again, the kinetic theory of matter tells us that the mean value of the kinetic energy of the resonator considered in § 9 ought, if the classical dynamics is true, to be given by

$$\overline{\beta \dot{\phi}^2} = RT,$$

so that formula (14), expressing the condition for equilibrium between the resonators and radiant energy, becomes

$$R(p)dp = \frac{RT}{\pi^2 V_3} p^2 dp, \quad . \quad . \quad . \quad . \quad (22)$$

which is identical with (21).

Radiation from Electron Orbits.

12. In § 10 we considered only the transfer of energy between electrons and radiation on the supposition that the electrons were absolutely free, and acted on only by the forces arising from the radiation. A somewhat different problem arises in the more natural case in which the free electrons are threading their way through the interstices of matter, and are in consequence experiencing accelerations and emitting radiation at each encounter with the atoms of the matter. The problem was first considered by Lorentz,† who found a formula giving the partition of radiant energy in the steady state for waves of great wave-length. Later the question was again attacked by the present writer,‡ who confirmed Lorentz's

* "Phil. Mag.," XVI., p. 353; also XVII., p. 890, and XVIII., p. 681.

† "On the Emission and Absorption by Metals of Rays of Heat of Great Wave-length," "Koninklijke Akad. van Wetenschappen," Amsterdam, April 24, 1903.

‡ "The Motion of Electrons in Solids," "Phil. Mag.," June, 1909, p. 773, and July, 1909, p. 209.

result by a different method, and showed how it could be extended to waves of all wave-lengths. The analysis of these Papers is too long to be reproduced here, even in abstract, but the final result obtained is that the partition of energy of all wave-lengths must, in the final state of equilibrium, be given by

$$R(p)dp = \frac{RT}{\pi^2 V^3} p^2 dp, \quad (23)$$

which, again, is identical both with (21) and (22).

13. The above formula gives the partition of radiant energy according to frequency, but it is easily transformed into one giving the partition according to wave-length. Let the energy within a range $d\lambda$ of wave-length be $\varphi(\lambda, T)d\lambda$, then, since

$\lambda = \frac{2\pi V}{p}$, the above formula becomes

$$\varphi(\lambda, T)d\lambda = 8\pi RT \lambda^{-4} d\lambda. \quad (24)$$

On comparison with formula (1) it is seen that the final partition of energy in the ether predicted by the classical dynamics is exactly analogous to that known to occur in a steady state in a gas. The sole difference lies in a multiplying factor 2, which is readily explained by the difference between sound-waves and light-waves (*cf.* § 14, below).

14. The physical interpretation of these formulæ is easily found. Consider any finite volume, v , of any homogeneous and continuous medium. The medium enclosed within this volume will be capable of executing a certain number of free vibrations, and associated with each free vibration will be its frequency $p/2\pi$ and the corresponding wave-length λ . When the wave-length is sufficiently small, the number of free vibrations for which λ lies within even a small range of values will be very great. Let us, in general, suppose that the number lying within a range $d\lambda$ is $f(\lambda)d\lambda$. Then, clearly, $f(\lambda)$ will be proportional to v , and hence, from a consideration of physical dimensions, since $f(\lambda)d\lambda$ is to be a pure number, it must be of the form

$$f(\lambda)d\lambda = Cv\lambda^{-4}d\lambda,$$

where C is a constant. In other words, the number of vibrations per unit volume of the medium of wave-length between λ and $\lambda + d\lambda$ is $C\lambda^{-4}d\lambda$. The determination of the constant C for any medium is not difficult.* It is found that for the vibra-

* "Phil. Mag.," July, 1905, p. 91; H. A. Lorentz, "The Theory of Electrons," § 73; also a purely mathematical Paper by H. Weyl, "Math. Annalen," LXXI., p. 441.

tions of sound in a gas $C=4\pi$, for the light vibrations in free ether $C=8\pi$, and for the elastic solid vibrations $C=12\pi$. The reason why these numbers are in the ratio 1 : 2 : 3 is obvious. In a gas there is only the one set of normal vibrations, in ether there are only transverse vibrations, but there are two independent transverse vibrations, corresponding to two planes of polarisation, for each normal vibration in the gas, and in the elastic solid there are both normal and transverse vibrations.

15. In the sound formula (1) given in § 5, namely,

$$4\pi RT\lambda^{-4}d\lambda,$$

we note that the number of vibrations within the range $d\lambda$ of wave-length is $4\pi\lambda^{-4}d\lambda$, and therefore *the average energy of each vibration is* RT . In the radiation formula

$$8\pi RT\lambda^{-4}d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

the number of vibrations is $8\pi\lambda^{-4}d\lambda$, so that *the average energy of each vibration is again* RT . Thus the classical mechanics require that, in the steady state of equilibrium, the average energy of each vibration shall be RT , whether in the ether or in a gas. A physical discussion of this is given later.

The Theorem of Equipartition of Energy.

16. It has now been seen how the general result can be obtained that in the steady state the average energy of each vibration is RT , whether the vibration is a sound vibration in a gas, or a light vibration set up by resonators, or by free electrons in ether, or by free electrons colliding with matter. This result is only part of a much more general result which can be obtained from the well-known theorem of equipartition of energy, a brief account of the proof of which may now be given, omitting all complications which have no bearings on the problems we are now concerned with.

Consider any dynamical system which will be supposed to move in accordance with the Newtonian laws, and let its condition be determined by n Lagrangian co-ordinates and the n corresponding momenta. Let these $2n$ quantities be denoted by $\theta_1, \theta_2 \dots \theta_{2n}$.

Then the condition of the system at any instant may be represented graphically by a point in an imaginary space of $2n$ dimensions, this point having for its Cartesian co-ordinates $\theta_1, \theta_2 \dots \theta_{2n}$. As the system follows out its natural motion this point will trace out a curve in the $2n$ dimensional space.

We may now suppose that the whole space is filled with representative points tracing out their appropriate curves, and in this way we can imagine that we have a graphical representation which enables us to study simultaneously all motions possible for our dynamical system.

According to the well-known theorem of Liouville,* the density of any group of points in this space does not change as the points follow out the paths descriptive of the natural motion of the system, provided this motion is in accordance with the Newtonian mechanics. For instance, if the moving representative points are initially sprinkled with uniform density throughout the space they will remain of uniform density for ever.

Suppose it is found that after the steady state has been reached—i.e., after the motion has gone on for so long that the influence of the initial conditions has been obliterated—the system invariably possesses some definite property P. This might be from one of two reasons: Either that the representative points tend in their motion to cluster in those regions of the generalised space in which the property P holds, or that the property P is common to the whole of the generalised space. But Liouville's theorem shows that the first of these cannot be the true reason. The property P must be common, then, to the whole of the generalised space. Strictly speaking, no property of any physical interest can be found which is common to absolutely every point in the generalised space, but a number of properties can be found which are true with very insignificant exceptions, these exceptions being such as would escape notice in experimenting. Thus we may say that the properties to be looked for in the steady state of a system are those which are common to the whole of the generalised space.

These somewhat abstract considerations may be illustrated by a perfectly non-dynamical concrete example.

Suppose that we have an army of a million men of average height 5 ft. 8 in. This army can be divided into two wings each of 500,000 men in approximately $10^{301.027}$ different ways. There will, perhaps, be a million ways of arranging the men so that the average heights in the two wings may differ by as much as 2 in.; there may be (say) 10^{100} ways in which the averages may differ by $\frac{1}{100}$ in.; there will be, perhaps, 10^{1000} ways in which the average will differ by $\frac{1}{1000}$ th of an inch. But

* Boltzmann, "Vorlesungen über Gastheorie," Vol. II., pp. 66, 67; or Jeans, "Dynamical Theory of Gases," p. 62.

for the majority of arrangements the average heights will be almost exactly equal. With the figures we have taken the chance will be $10^{300,000}$ to 1 that the average height in the two wings will be the same to within $\frac{1}{1000}$ th of an inch. It is not true to say that for all arrangements of the men the average heights in the two wings will be only imperceptibly different, and yet the odds are $10^{300,000}$ to 1 against this statement being untrue if the men are arranged at random.

So, in the generalised space under consideration, there will be no property absolutely true of the whole space, but a number of properties can be found which are true for all points in the space except for a number which constitute a perfectly insignificant fraction of the whole. In particular, the following is easily shown to be such a property.

Let two groups of terms be taken out of the expression for the energy, each consisting of a very large number (p , q) of squared terms. Then the property which is true within the limits explained is that the average value of each term in the group of p terms is equal to the average value of the q terms. If, as in the kinetic theory of gases, we take the average value of terms in either group to be $\frac{1}{2}RT$, then the value of the group of p terms will be $\frac{1}{2}pRT$, while that of the group of q terms will be $\frac{1}{2}qRT$. This is, in effect, the theorem of equipartition of energy.*

17. It will be seen at once that this result embraces all the results which have been obtained in this chapter. For let the system under consideration consist of ether together with matter of all kinds. The number of vibrations of the ether of wave-length between λ and $\lambda+d\lambda$ will be $8\pi v\lambda^{-4}d\lambda$, where v is the volume of ether considered, and each vibration will give rise to two squared terms in the energy, one kinetic and one potential. The total number of squared terms representing the energy of all these vibrations will be $16\pi v\lambda^{-4}d\lambda$, and therefore their energy will be equal to this number multiplied by $\frac{1}{2}RT$, or to $8\pi RTv\lambda^{-4}d\lambda$. Dividing by v to reduce to energy per unit volume of ether, we obtain for the radiant energy of wave-length between λ and $\lambda+d\lambda$

$$8\pi RT\lambda^{-4}d\lambda,$$

which is identical with formula (24).

* For references to the various proofs which have been given see Jeans, "Dynamical Theory of Gases," Ch. V., or "La Théorie du Rayonnement et des Quanta" (Gauthier-Villars, Paris, 1912), p. 71. Detailed proofs of the theorem will also be found in both these places.

This formula was given by Lord Rayleigh and the present author in 1900 as being the formula which ought, on the Newtonian mechanics, to govern the partition of energy in the spectrum. It cannot be the true law, for the total energy obtained by integrating from $\lambda=0$ to $\lambda=\infty$ would be infinite for any finite value of T . And if the total energy were finite the only possible value for T would be $T=0$.

This, in fact, is the prediction of the classical mechanics as to the final steady state. We are led to expect that all the energy of the matter will be dissipated away into radiation in the ether, just as in the analogies of §§ 4 and 5, where it was seen that a continuous medium had the capacity of extracting all the kinetic energy from a system immersed in it. It is to escape from this necessary consequence of the classical mechanics that the quantum-theory has been brought into being.

Attempts to Reconcile Radiation Phenomena with the Classical Mechanics.

18. At this stage, before an account is given of the quantum-theory, it is appropriate that some reference should be made to the various attempts at reconciling the observed radiation formula with the Newtonian mechanics. A report such as the present ought to aim at explaining the various opinions held on controversial matters, in order that the reader may be amply supplied with materials for forming his own judgment. The recent discussion at the Birmingham meeting of the British Association made it abundantly clear that the quantum-theory is far from being regarded as inevitable yet by many of the English school of physicists. The following accounts of the remarks made by Sir J. Larmor and Prof. Love, in addition to being of great intrinsic interest, will sufficiently indicate what variety of views is possible.*

“Sir J. Larmor derived the impression from the trend of the discussion that it would turn out that in the new low-temperature determinations there was nothing in direct conflict with the classical dynamical principles. The essential argument for equipartition among vibrational types of energy is, briefly, that these types enter similarly into the total energy, and thus, other things being indifferent, there is no reason that can be assigned to the contrary. They enter similarly merely

* “British Association Report” (1913), Birmingham, p. 385.

because the energy is a sum of squares of their 'momentoids.' But other things may not be indifferent; for example, in the kinetics of a rotating atmosphere the distribution of energy must be modified so as to maintain constancy of the angular momentum as well as of the energy, giving as the result equipartition relative to the rotation instead of absolutely. Moreover, in an isolated region of ether there is no way open for any interchange of energy at all between one type of vibration and another; here also other things are *not* indifferent. The exchange must be effected through the mediation of material molecules. It is true that a single electron, moving erratically between complete reflections from the ideal impervious walls of the chamber, would suffice; but the structure of an electron, including the mechanisms by which it exchanges energy with the ether, is totally unknown. Such a fundamental fact as the pressure of radiation is involved in that structure; we can only establish it theoretically as pressure on systems of electrons; it must be transmitted by the ether in some way, but we do not know how, except by speculating, for it is a second-order phenomenon not involved in the Maxwellian linear scheme of equations. In the very intense kinetic phenomena in the mechanism of the electrons or molecules, by which they serve to transfer energy from one type of ethereal vibration to other types, the energy must be expressible as a sum of squares of definite momentoids if the transfer is to lead ultimately to equipartition. This restriction in its form is unlikely; the transfer may even be of a discontinuous character, involving release of electrons into freedom. The Planck formula for the constitution of natural free radiation may be obtained by statistical reasoning, strictly on the lines of Boltzmann's entropy theory for gases, in which atoms or vibrators are not considered at all, but the pressure of radiation is introduced instead, as I have tried to show ("Proc. Roy. Soc.," 1906); the only implication is that the process of interchange of ethereal energy between different vibrational types, by the mediation of matter, though unknown, must be such as to provide a pressure of radiation. If, then, there is no reason to press equipartition as regards free natural radiation, the atomic vibrations, which are set up by its agency and must be in equilibrium with it, are also absolved therefrom.

"The new knowledge relating to specific heats at very low temperatures has already suggested most interesting speculations and tentative adjustments, and will certainly lead to

definite expansion of our theoretical schemes ; but it can be held that there is nothing in it that is destructive to the principles of physics which have led to so rich a harvest of discovery and synthesis in the past."

" Prof. A. E. H. Love : I am unable to accept the view that, in order to account for the facts about radiation, existing theories of dynamics and electro-dynamics need to be supplemented by the theory of quanta. Part of the evidence in favour of this view has been derived from an application of the principle of equipartition of energy to a system consisting of ether and matter in an enclosure bounded by perfectly reflecting walls. Such a system has an infinite number of degrees of freedom, and the principle of equipartition cannot be applied without modification to any such system. The ethereal kinetic energy would be expressed by an infinite series of the form

$$u_1 + u_2 + u_3 + \dots \text{ ad inf.},$$

in which there is one term answering to each degree of freedom, and the order of the terms is that of increase of the corresponding frequencies. In order that an infinite series may represent ethereal kinetic energy, or anything else, it is necessary that it should be convergent. In order that it may be convergent it is necessary that all the terms which are far advanced in the order of the series should be very small compared with some of those which precede them. It is, therefore, impossible for all the terms to be equal as required by the principle of equipartition. If, however, the principle of equipartition is limited by the principle of convergence, it yields some information as to the distribution of energy in the spectrum of a black body. In so far as it is legitimate to regard the infinite series, by way of approximation, as the sum of a large but finite number of terms, the principle of equipartition should be applicable, also as an approximation, and it yields Lord Rayleigh's experimentally verified formula for the emissivity answering to long waves. The principle of convergence shows, on the other hand, that for short waves the curve obtained by plotting emissivity against wave-length should fall towards the origin, as it is known to do. But this principle yields no information as to the position in the spectrum of the longest waves for which Lord Rayleigh's formula fails to give a valid approximation.

" The arguments on which the theory of quanta was founded cannot be regarded as satisfactory. Indeed, the most convincing evidence in favour of the theory would seem to be the

agreement with experiment of M. Planck's formula, according to which the emissivity of a black body is given as a function of the wave-length λ and the absolute temperature T , by an expression of the form

$$A\lambda^{-5}(e^{B/\lambda T} - 1)^{-1},$$

where A and B are properly determined constants. It may, therefore, be pertinent to remark that from a mathematical point of view there must be infinitely many formulæ which would agree equally well with the experiments. In illustration of this statement, it may be mentioned that a formula proposed recently by A. Korn, according to which the emissivity of a black body would be given by an expression of the form

$$C\lambda^{-6}T^{-1}(e^{D/\lambda T} - 1)^{-2},$$

where C and D are properly determined constants, when tested arithmetically over a wide range, yields results showing just about as good an agreement with the facts as Planck's. It may be, however, that there is no simple formula, like those of Planck and Korn, which is applicable to all wave-lengths. However this may be, there seems to be no sufficient reason for regarding Planck's formula as expressing a law of Nature.

"In further illustration of the contention that the resources of the ordinary theories are not exhausted, it may be pointed out that it is possible to extend to some additional cases the calculation, first carried out by H. A. Lorentz in the case of long waves, of the emissivity of a thin metal plate. He supposed the radiation to be generated in collisions between free electrons and atoms, and calculated the emissivity for waves of periods long compared with the times occupied in describing free paths. For this calculation he required to evaluate approximately a certain integral. Such an evaluation can be effected also in the case of waves which have their periods comparable with the times occupied in describing free paths, and, for a number of laws of variation of the acceleration during a collision, in the case of waves which have their periods comparable with the times occupied by collisions. As the wave-length diminishes the emissivity of the thin plate at first increases, then reaches a maximum, and finally diminishes to zero; as the temperature rises the wave-length answering to the maximum emissivity diminishes, as would be expected. But there is no simple analytical formula which represents the emissivity of the thin plate over the whole range of wave-lengths."

To the remarks of Prof. Love the following reply was made by Prof. Lorentz :—

“Prof. Lorentz : In reply to Prof. Love’s interesting remarks, I should like to say that it is precisely one of the objects of the physical theory of radiation to explain why the energy of the black radiation can be represented by a convergent series. The old theories lead to a different result, but this in itself would not be a physical contradiction or impossibility ; it would simply mean that all energy will in the end be transferred to the ether and that it will continually take the form of shorter waves, a really final state never being reached. Our aim must be to account for a true state of equilibrium, in which there is a finite ratio between the parts of the energy that are found in a ponderable body enclosed in an envelope and in the surrounding ether. We shall also have to assign a physical meaning to the universal constant h occurring in the formula by which Planck calculates this ratio.”

19. The following additional comments may also be made with reference to Prof. Love’s suggestions. As regards the convergence of Prof. Love’s infinite series, we may suppose those terms which represent vibrations in the ether to be arranged in order of descending wave-length. It will then be seen that the equations of the classical dynamics demand that the energy should, so to speak, be transferred along the terms of the series from left to right, and no steady state can be attained until the terms are all equal. Now the time required, on the classical dynamics, for the energy to reach the more distant terms admits of approximate calculation, and it can be shown that before we have got very far along the series this time becomes a matter of millions of years.* Let us then cut off the tail of Prof. Love’s infinite series, and retain, say, only the first 10^{10} terms ; this gives us a finite series of terms which, until after the lapse of millions of years, is perfectly capable of representing physical conditions, and for which purely mathematical questions of convergence have no meaning.

The suggestion that a satisfactory radiation formula might be obtained by the old mechanics from an analysis of electron orbits is one to which a good deal of attention had already been given. As has been seen, the only formula which can possibly be obtained is Lord Rayleigh’s law (§§ 12, 17), unless it is assumed that the observed law is not a true final state of thermodyna-

* Cf. “The Dynamical Theory of Gases,” Chapter IX.

mical equilibrium. If, however, it is supposed that the emitted radiation of the highest frequencies is in some way drained off or allowed to escape, so that the density of radiation in the ether always remains very small, then it is possible to obtain a definite law, which, as Love remarks, shows some of the characteristics of the observed radiation law. Instead of obtaining the Rayleigh formula

$$8\pi RT\lambda^{-4}d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

we obtain* a formula of the type

$$8\pi RT\lambda^{-4}f\left(\frac{c}{\lambda}\right)d\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

in which c is a quantity such that $\frac{c}{2\pi V}$ is comparable with the time of a collision between the electron and an atom. From what has already been said, it is clear that for very long waves

$f\left(\frac{c}{\lambda}\right)$ must approximate to unity, while, if the collisions are all of equal duration, it can be shown that, when λ is very small, $f\left(\frac{c}{\lambda}\right)$

will tend to zero in the same way as $e^{-\frac{c}{\lambda}}$. Making the assumption that the motion of each electron is made up of a series of exactly similar collisions, separated by rectilinear free-paths, Sir J. J. Thomson† has arrived at the formula

$$8\pi RT\lambda^{-4}e^{-\frac{c}{\lambda}}d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

which is, of course, a special case of (27).

The following considerations at once are suggested :—

I. To reconcile formula (27) with Wien's law (3), c must vary as $\frac{1}{T}$, so that the duration of a collision must be exactly pro-

portional to $\frac{1}{T}$. This would be the case if the atoms were centres of force repelling according to the law of the inverse cube,‡ but this is not a condition which can be easily reconciled with what is known about the structure of atoms and the motion of electrons.

* "La Th'orie du Rayonnement et les Quanta," p. 69; and J. H. Jeans, "Phil. Mag.," July and August, 1909.

† "Phil. Mag." 14 (1907), p. 225.

‡ J. J. Thomson, *l.c. ante*.

II. It is, of course, possible to find the value of c which would be required to make formula (27) agree with Planck's formula. At ordinary temperatures, the time of collision would have to be of the order of 10^{-14} seconds. Remembering that the velocity of the electron is of the order of 10^7 , it is clear that this time of collision is too large to reconcile with what is known about molecular or atomic dimensions.*

III. For formula (27) to agree with the observed black-body radiation, the value of c , and the time of a collision, would have to be exactly the same for all substances, a condition which cannot be reconciled with the known diversity of structure of different substances.

IV. The experiments of Richardson and Brown† have shown that the velocities of the electrons in a solid are distributed according to Maxwell's law, so that the values of c must be different for different electrons and for different collisions. On intergating for all possible velocities, it is found that the limiting form for $f\left(\frac{c}{\lambda}\right)$, when λ is very small, is not proportional to $e^{-\frac{c}{\lambda}}$ but to $e^{-\sqrt{\frac{c}{\lambda}}}$, and this cannot be reconciled with observation.‡

* "Phil. Mag." 20, (1910), p. 651.

† "Phil. Mag." 16 (1908), p. 353.

‡ "Phil. Mag." 20 (1910), p. 650.

CHAPTER III.

THE DEVELOPMENT OF THE QUANTUM-THEORY.

20. The last chapter showed that, consistently with the assumption of thermodynamical equilibrium, the Newtonian system of equations could lead to only one formula for the partition of radiant energy, namely, $8\pi RT\lambda^{-4}d\lambda$, a formula which does not agree with experiment. In the present chapter it will be explained how Planck, starting from conceptions entirely different from those of the Newtonian mechanics, has arrived at a radiation formula which is in agreement with observation, and how Poincaré has shown that the observed radiation formula can be derived from only one set of physical assumptions, namely, those of the quantum-theory.

In the ordinary theory of gases, the "probability" that a system shall have its co-ordinates (p_1, p_2, \dots) and momenta (q_1, q_2, \dots) within a range $dp_1 dp_2 \dots dq_1 dq_2 \dots$ is found to be of the form

$$Ae^{-2hE} dp_1 dp_2 \dots dq_1 dq_2 \dots,$$

where E is the energy of the system in this configuration, A is a constant and h is given by $2hRT=1$. Hence, if ε is any amount of energy, the probabilities of the system having energies $0, \varepsilon, 2\varepsilon, \dots$, will stand in the ratios

$$1 : e^{-2h\varepsilon} : e^{-4h\varepsilon} : \dots$$

Strictly speaking, the probabilities we are discussing are not those of the system having energies $0, \varepsilon, 2\varepsilon, \dots$ but of its co-ordinates lying within equal infinitesimal ranges of values $dp_1 dp_2 \dots dq_1 dq_2 \dots$ surrounding these energies, but this complication is immaterial for our present purpose.

Suppose that we are considering a very great number, M , of vibrations, and suppose that of these N have zero energy. Then the number which may be expected to have energy ε will be $Ne^{-2h\varepsilon}$, the number which may be expected to have energy 2ε will be $Ne^{-4h\varepsilon}$, and so on. If we suppose, purely as a conjectural hypothesis at present, that all of the M vibrations have

their energies equal to one or other of the values $0, \varepsilon, 2\varepsilon, \dots$ then we must have

$$M = N(1 + e^{-2h\varepsilon} + e^{-4h\varepsilon} + e^{-6h\varepsilon} + \dots) = \frac{N}{1 - e^{-2h\varepsilon}}. \quad (29)$$

The total energy of all these vibrations must be

$$Ne^{-2h\varepsilon} \cdot \varepsilon + Ne^{-4h\varepsilon} \cdot 2\varepsilon + Ne^{-6h\varepsilon} \cdot 3\varepsilon + \dots,$$

of which the value, on summing and using relation (29), is found to be

$$\frac{M\varepsilon}{e^{2h\varepsilon} - 1} \cdot \dots \dots \dots (30)$$

If the particular vibrations are those of wave-length between λ and $\lambda + d\lambda$ in a unit volume of ether, the value of M must be taken to be (*cf.* § 14) $8\pi\lambda^{-4}d\lambda$, and formula (30) assumes the form

$$8\pi\lambda^{-4}d\lambda \frac{\varepsilon}{e^{2h\varepsilon} - 1} \cdot \dots \dots \dots (31)$$

We can pass to the problem contemplated in § 15 by passing to the limit $\varepsilon = 0$; for the vibrations are supposed capable of having energies $0, \varepsilon, 2\varepsilon, 3\varepsilon, \dots \infty$, which, when $\varepsilon = 0$, means simply that the energy can have any value. Now, when ε is small, the limiting value of $\frac{\varepsilon}{e^{2h\varepsilon} - 1}$ is $\frac{1}{2h}$ or RT , so that formula (31) reduces to

$$8\pi RT \lambda^{-4} d\lambda \cdot \dots \dots \dots (32)$$

This agrees with formula (25), as of course it should, and so does not agree with observation. Formula (31), in which ε is not taken equal to zero, may be put in the form

$$8\pi RT \lambda^{-4} d\lambda \times \frac{\frac{\varepsilon}{RT}}{e^{\frac{\varepsilon}{RT}} - 1}, \quad \dots \dots \dots (33)$$

and so will agree with observation (*cf.* § 7) if

$$\varepsilon = h\nu, \quad \dots \dots \dots (34)$$

where h is now Planck's constant and ν is the number of vibrations per second.

21. This is probably the shortest way of illustrating the connection between Planck's fundamental equation (34) and his radiation formula (4). There are obviously, however,

grave objections to supposing that the energies of the vibrations in the ether must be multiples of ϵ . For this involves that these energies can only alter by sudden jumps of amounts which are themselves multiples of ϵ , and the occurrence of these jumps would seem to be inconsistent with the supposition that the energy is spread throughout the whole of the ether.

The original method of Planck* was based on somewhat different physical ideas. Suppose that the M vibrations considered in § 20 are the vibrations of M resonators, each of frequency ν . Their total energy will be given by expression

(30), so that the average energy of each vibrator will be $\frac{\epsilon}{e^{2h\nu} - 1}$, and the average kinetic energy will be one-half of this, or

$$\frac{1}{2}RT \times \frac{x}{e^x - 1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

where $x = \frac{\epsilon}{RT}$. The conditions for equilibrium between resonators and ether have been considered in § 9; we note that the average kinetic energy of a resonator must now, from formula (35), be supposed to be $\frac{x}{e^x - 1}$ times what it was supposed to be in § 9, and the result is that the radiation formula is equal to that previously found multiplied by $\frac{x}{e^x - 1}$. In other words, the radiation formula now obtained is that of Planck.

22. It is in this way that Planck obtains his formula, but this method also is open to objections. For, in considering the partition of energy between the various resonators, it is assumed that the energy can only vary by jumps of amount ϵ , while, in considering the partition of energy between resonators and ether, it has to be assumed, as in § 9, that the energy of the resonators can vary continuously. Moreover, it has to be assumed also that the energy of the various vibrations in the ether can vary continuously, and, this being so, the condition for equilibrium between ether and, for instance, free electrons, would be expected to be that obtained in § 10. In other words, we should expect that the resonators would, so to speak, strive to set up Planck's partition of radiant energy, while the free electrons and other mechanisms would strive to establish the equi-partition formula (32) of Lord Rayleigh. The result

* "Annalen der Physik," 4 (1901), p. 556.

would be a compromise between the two laws, as a result of which the final law would differ for different substances (*cf.* § 8), while the physical processes by which it was determined would violate the second law of thermodynamics.

The present chapter is intended to deal only with the mathematical development of the quantum-theory, so that the physical difficulties just mentioned may be reserved for later discussion (Chapter VII. below).

23. The discussion of another mathematical problem finds a suitable place in the present chapter. The assumption that changes in the energy of resonators or vibrations follow the Newtonian laws leads, as we have seen, to the formula of Lord Rayleigh, while the assumption that these changes occur by jumps of amount $\varepsilon = h\nu$ leads to Planck's law. The converse problem demands consideration, at least in the special case of Planck's law, which is known to agree with observation. The problem is the following: Given that the final partition of energy is that given by Planck's law, what laws of motion must be postulated for the system in order to obtain this law?

This problem has been solved with great completeness by Poincaré.* The result obtained is, in brief, that no system can possibly lead to Planck's law, except one in which the assumption of the quantum-theory is satisfied: "L'hypothèse des quanta est la seule qui conduise à la loi de Planck."† Unfortunately Poincaré's Paper is of such an abstruse mathematical nature that it is impossible to do any sort of justice to it in an abstract; the reader who wishes to understand it must turn to the original Paper.

The following investigation of the same question,‡ although less complete than that of Poincaré, is based on similar ideas, and leads to the same conclusions.

Consider the system discussed in § 16, and let the values of the quantities $\theta_1, \theta_2, \dots$ be represented in a generalised space, just as before; and, again, let all possible states and changes of the system be represented by swarms of moving points.

In the former investigation, the systems represented by the moving points were supposed to obey the laws of the old mechanics. It followed that there was no concentration of the swarms of points; they moved indifferently through the whole

* "Journal de Phys.," January, 1912.

† *L.c.*, p. 37.

‡ "Phil. Mag.," December, 1910, p. 943.

space, and, as equipartition was a property of the whole space, it followed that equipartition ultimately ensued for all the systems.

We are now searching for a final result different from equipartition, so that we must no longer suppose that the swarms of points move without any concentration taking place, as they would do if the Newtonian laws held. Whatever laws or systems of equations govern the motion of the system, we must suppose some definite law of causation to hold—this is a necessary condition for the problem being capable of discussion at all. A system of particles endowed with free-will would not be a fit subject for mathematical treatment. It must be supposed, then, that the moving points in the generalised space follow definite tracks through the space, and, this being so, it is possible so to arrange the initial swarm of particles that the density at any point of the space remains always the same,* and does not vary with the progress of the motion. It is now only necessary to consider this permanent arrangement of density.

Now, if the density of these swarms of points differed only by finite amounts, we should still be led to equipartition of energy and the radiation formula (32) of the last chapter. For, always excepting infinitesimal fractions, equipartition holds for all of the generalised space, and so, if the density were finite everywhere, would hold for all the representative points. The only way of avoiding the equipartition formula is to suppose that the density of the swarms of points must be zero throughout the whole, except for infinitesimally small regions, of the generalised space. There must be isolated small regions R_1, R_2, \dots in the generalised space occupied by dense swarms of points; in all other regions the density of points must be zero or infinitesimal. And, in order to satisfy the hydrodynamical equation of continuity in the generalised space, the motion of the points must consist of sudden jumps from one of the regions R_1, R_2, \dots to another. It appears in this way that, as soon as we seek to avoid the equipartition formula (32), we are compelled to assume motion involving discontinuities of some kind.

24. This result is so entirely identical with that obtained by Poincaré that we may, without break of thought, pass to his discussion of it.†

* The argument in more detail will be found in Poincaré's Paper or the Paper already referred to, "Phil. Mag.," December, 1910.

† "Dernières Pensées," p. 185. (I have translated freely.)

“ All the states of the system which are represented in any one of these regions [called R_1 , R_2 above] are indistinguishable from one another ; they constitute one single definite state, so that we are led to the following proposition, one which is more definite than that of M. Planck, but not, I think, contrary to his ideas :—

“ *A physical system is only susceptible of a finite number of distinct states ; it jumps from one of these states to another without passing through a continuous series of intermediate states.*

“ Suppose, to take a simplified illustration, that the state of the system depended only on three co-ordinates, x , y , z , so that we could represent it by a point in ordinary space. The swarm of points representing the different possible states will no longer fill the whole of this space or a region of this space in the ordinary sense ; there will be a great number of isolated points scattered through space. These points, it is true, are very close together, which gives us the illusion of continuity.*

“ All these states must be regarded as equally probable. Indeed, if we admit determinism, to each of these states must necessarily succeed another state, which is just equally probable, since it is certain that the first is followed by the second. Thus one can see step by step that if we start from any initial state, all the states to which we shall arrive in time must be equally probable ; all others must not be regarded as possible states at all.

“ But our representative isolated points must not be scattered in space in any fashion we please ; they must be distributed in such a way that in observing them with our coarse-grained appliances (*avec nos sens grossiers*) we have been led to believe in the ordinary dynamical laws, in particular in the laws of Hamilton. A comparison which approaches nearer to the reality than might be thought will make this clearer. The appearance of a liquid suggests at first that its structure is continuous ; observation shows that the liquid is incompressible, so that the volume of any portion of its matter remains constant. Certain reasons then lead us to suppose that this liquid is composed of molecules, very small and very numerous,

* That is to say, when we look at them on the scale of the ordinary mass-phenomena of nature. But in considering phenomena concerned with atoms, electrons, &c., we assume, so to speak, a mental microscope, and on looking at the points through a mental microscope of this power, they are seen to be widely separated. How wide, judged on this scale, is the gap that separates one point from its nearest neighbour will be clear from the calculations given in § 29 of the present report.—J. H. J.

but discrete. We cannot now suppose the distribution of these molecules arranged in any way we fancy ; the incompressibility of the liquid compels us to suppose that two equal small volumes contain the same number of molecules. In his distribution of possible states, M. Planck finds himself limited in a similar way.

“ One might, it is true, imagine hybrid hypotheses. Let us return to the system which we supposed specified by three co-ordinates, so that its state could be represented by a point in space. The regions occupied by the representative points might be neither a continuous region in space nor a collection of isolated spots : it might be composed of a great number of small distinct surfaces, or of small distinct curves. It might be, for instance, that one of the material points of a system might describe only certain trajectories, and might describe them in a continuous manner except when it jumps from one trajectory to another under the influence of its neighbours* ; this might be the case with the resonators considered above. Or, again, the state of the ponderable matter might vary in a discontinuous way, with only a finite number of possible states, while the state of the ether varied in a continuous manner. Nothing in all this would be incompatible with the ideas of M. Planck.

“ But the reader will doubtless prefer the first solution, a solution which is free from all these bastard hypotheses. Only he must note the consequences which it involves. What has been said must apply to any isolated system whatever, and even to the universe as a whole. Thus the universe would jump suddenly from one state to another, but in the interval between it would stand at rest. The different instants during which it stayed in the same state could not be distinguished from one another, so that we should be led to the discontinuous variation of time, *to the atom of time.*”

25. All this has followed merely from the hypothesis, or the fact, that the energy in the spectrum does not obey the equipartition formula of Lord Rayleigh. Let us next consider what particular form of discontinuities must be postulated in order to arrive at Planck's law.

Let the total energy E of the system be supposed made up of separate parts E_1, E_2, \dots , this division being made in such a way that E_1 depends only on one certain group of the

* Compare Bohr's theory of the structure of the hydrogen atom ; § 37 of the present report.

co-ordinates $\theta_1, \theta_2, \dots$, E_2 depends only on a certain other group of co-ordinates and so on, no one co-ordinate entering into more than one group.

Let $W_{E_1}dE_1$ denote the proportion of the whole number of points for which E_1 has a value between E_1 and E_1+dE_1 ; let $W_{E_2}dE_2$ denote the proportion for which E_2 has a value between E_2 and E_2+dE_2 , and so on. Then* the proportion for which E_1, E_2, \dots all lie within these specified ranges may be denoted by $WdE_1dE_2\dots$ and will be given by

$$WdE_1dE_2\dots=(W_{E_1}dE_1)(W_{E_2}dE_2)(\dots)\dots$$

in which W_{E_1} will be a function of E_1 only, W_{E_2} of E_2 only, and so on.

The most likely values for E_1, E_2, \dots to have will, of course, be those which make W a maximum, or $\delta W=0$. We have

$$\frac{\delta W}{W} = \frac{1}{W_{E_1}} \frac{\partial W_{E_1}}{\partial E_1} \delta E_1 + \frac{1}{W_{E_2}} \frac{\partial W_{E_2}}{\partial E_2} \delta E_2 + \dots \quad (36)$$

Whatever system of laws governs the motion we may, on experimental grounds, suppose the conservation of energy to be satisfied so that the total energy E retains the same value throughout. Now

$$E=E_1+E_2+\dots,$$

so that

$$\delta E = \delta E_1 + \delta E_2 + \dots = 0, \quad \dots \quad (37)$$

and the condition that δW , as given by equation (36), shall vanish when $\delta E_1, \delta E_2, \dots$ are subject to the limitations expressed by equation (37) is

$$\frac{1}{W_{E_1}} \frac{\partial W_{E_1}}{\partial E_1} = \frac{1}{W_{E_2}} \frac{\partial W_{E_2}}{\partial E_2} = \dots \quad (38)$$

If one part of the system, say that of energy E_s , is supposed to be a gas thermometer, the value of the corresponding differential $\frac{1}{W_{E_s}} \frac{\partial W_{E_s}}{\partial E_s}$ can be readily calculated and is found to be $\frac{1}{RT}$. Thus, the most likely set of values for E_1, E_2, \dots are those given by

$$R \frac{\partial}{\partial E_1} (\log W_{E_1}) = R \frac{\partial}{\partial E_2} (\log W_{E_2}) = \dots = \frac{1}{T}, \quad \dots \quad (39)$$

$$\text{or} \quad \frac{\partial S}{\partial E_1} = \frac{\partial S}{\partial E_2} = \dots = \frac{1}{T}, \quad \dots \quad (40)$$

* For details see the Paper already referred to "Phil. Mag.," December, 1910.

where $S=R \log W$. It is now possible to identify S with the entropy*; the most likely values for E_1, E_2, \dots are simply those which make the entropy a maximum. It is easily shown that, for any system consisting of an enormously great number of parts, the regions in the representative space for which W is actually a maximum are enormously greater than all the others together. Thus, $\delta W=0$ or $\delta S=0$ expresses a true steady state. Since $S=R \log W$, it is the state simply in which the entropy is a maximum. The equations which express this are equations (40), which are now seen to be merely the expression of the second law of thermodynamics.

26. To examine what conditions will lead to Planck's law for the steady state, we have simply to identify the condition expressed by equation (40) or (39) with that expressed in Planck's formula.

According to Planck's formula (30), the energy E_1 of M vibrations of frequency ν vibrations per second is given by

$$E_1 = \frac{M\varepsilon}{e^{\varepsilon/kT} - 1},$$

where $\varepsilon = h\nu$; whence

$$\frac{1}{T} = \frac{R}{\varepsilon} \log \left\{ 1 + \frac{M\varepsilon}{E_1} \right\},$$

and, from relations (39),

$$\frac{1}{T} = R \frac{\partial}{\partial E_1} (\log W_{E_1}).$$

Thus
$$\frac{\partial}{\partial E_1} (\log W_{E_1}) = \frac{1}{\varepsilon} \log \left(1 + \frac{M\varepsilon}{E_1} \right),$$

giving on integration

$$\log W_{E_1} = \left(M + \frac{E_1}{\varepsilon} \right) \log \left(M + \frac{E_1}{\varepsilon} \right) - \frac{E_1}{\varepsilon} \log \frac{E_1}{\varepsilon} + \text{cons.}$$

Write P for E_1/ε and use Stirling approximation for factorials, and we obtain

$$W_E = C \frac{(M+P)!}{P!},$$

where C is a constant. But $\frac{(M+P)!}{P!}$ is the number of ways in which P articles can be put into M pigeon-holes, or, for our

* Boltzmann, "Vorlesungen über Gastheorie," I., § 6.

present purpose, is the number of ways in which P units of energy can be distributed between M vibrations capable of holding energy. Thus Planck's formula is obtained by supposing that the total energy E_1 is divided into P units (each of amount ε or $h\nu$, since $P = \frac{E_1}{\varepsilon}$) and that these are distributed among the M vibrations. Moreover, it is readily seen that this way of arriving at Planck's formula must be unique.

27. This result is the same as is arrived at in Poincaré's Paper, referred to above,* but Poincaré's method is one which makes it possible to proceed one stage further. Planck's law, if absolutely true, must, as has been seen, require the discontinuities of the theory of quanta. But, as Poincaré remarks,† a law found experimentally is never more than an approximation. Could we then imagine laws such that their differences from Planck's law would be within the errors of observation, but which would at the same time lead to a continuous system of dynamical laws?

This question has already been answered in § 23, and in Poincaré's Paper a second decided negative is again given. It is shown that no small, or even finite, departures from Planck's law will dispose of the necessity for discontinuity. Poincaré shows definitely and conclusively that the mere fact that the total radiation at a finite temperature is finite (the crucial fact referred to in § 2) requires that the ultimate motion should be in some way discontinuous—‡

“Quelle que soit la loi du rayonnement, si l'on suppose que le rayonnement total est fini, on serait conduit à une fonction présentant des discontinuités analogues à celles que donne l'hypothèse des quanta.”

It seems then to be abundantly proved that the transfer of energy must in some way take place by jumps or jerks of amount $\varepsilon = h\nu$, but mathematical analysis gives no indication as to the physical nature of these processes. The physical problem as to when, where and how the jumps occur can be solved with much less certainty than the mathematical problem of which the solution has predicted the occurrence of the energy jumps with a high degree of certainty. The consideration of the physical problem is deferred to the last chapter;

* “Journal de Physique,” January, 1912.

† *L.c.*, p. 27.

‡ *L.c.*, p. 29.

we now proceed to consider some purely numerical consequences of the mathematical solution which has been obtained.

28. The formula given by the Newtonian mechanics for the partition of black-body radiation was

$$8\pi RT\lambda^{-4}d\lambda, \dots \dots \dots (41)$$

while the formula given by the quantum-theory is the same formula multiplied by

$$\frac{x}{e^x - 1} = \frac{1}{1 + \frac{1}{2}x + \frac{1}{6}x^2 + \frac{1}{24}x^3 + \dots},$$

in which $x = \frac{\epsilon}{RT} = \frac{h\nu}{RT}$. From the above expansion it is clear that the energy given by Planck's formula is always less than that given by formula (41), and the divergence between the two formulæ increases as x increases—i.e., as we pass to higher frequencies or lower temperatures. The following table gives values of $x/(e^x - 1)$ for different values of x :—

| x . | $x/(e^x - 1)$. | x . | $x/(e^x - 1)$. |
|-------|-----------------|-------|-----------------|
| 0.0 | 1.000 | 2.0 | 0.313 |
| 0.2 | 0.903 | 2.4 | 0.239 |
| 0.4 | 0.813 | 2.8 | 0.181 |
| 0.6 | 0.730 | 3.2 | 0.136 |
| 0.8 | 0.653 | 3.6 | 0.101 |
| 1.0 | 0.582 | 4.0 | 0.0764 |
| 1.2 | 0.517 | 4.5 | 0.0505 |
| 1.4 | 0.458 | 5.0 | 0.0339 |
| 1.6 | 0.405 | 6.0 | 0.0149 |
| 1.8 | 0.357 | 7.0 | 0.0064 |

A graphical representation of Planck's formula and of formula (41), both arranged according to *frequency*, is given in Fig. 1, the thin line representing formula (41) and the thick line the formula of Planck. The characteristic difference between the two formulæ is, of course, that formula (41) increases indefinitely as the frequency increases, whereas Planck's formula attains a maximum, and then very rapidly falls off again to zero.

29. It is found that Planck's formula represents the experimentally observed distribution of energy if

$$h = 6.6 \times 10^{-27} \text{ ergs} \times \text{seconds.}$$

The value of the quantum of energy for any wave-length can be found at once. For the D-lines, $\nu = 5 \times 10^{14}$, so that

$$\epsilon = h\nu = 3.3 \times 10^{-12} \text{ ergs.}$$

This may be compared with the energies met with in the theory of gases. At 0°C . $RT=3.6 \times 10^{-14}$ ergs, so that the energy of an atom of mercury vapour at 0°C . is 5.4×10^{-14} ergs, and the quantum of yellow light is about that of *sixty* atoms of mercury, or other monatomic gas, at 0°C .

Again, the energy per atom of a hot solid is $3RT$, or $4 \times 10^{-16}T$. The radiation emitted by a solid at temperature T has its

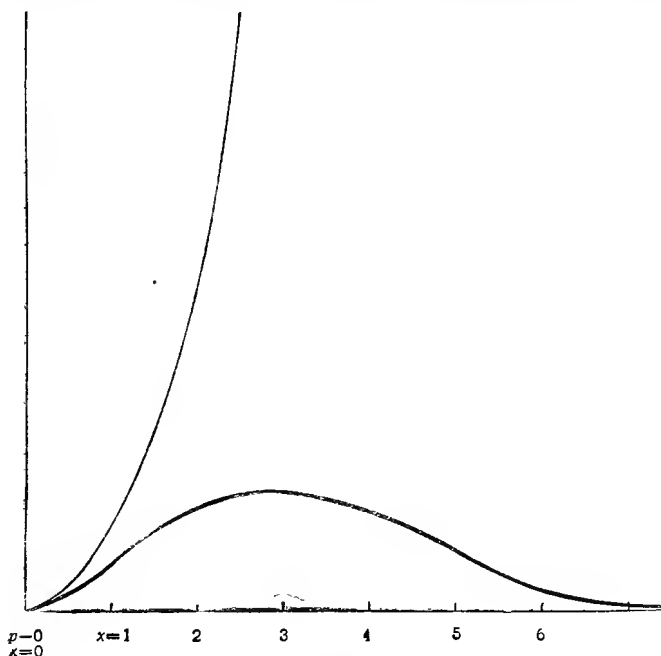


FIG. 1.

maximum ordinate λ_{\max} given by $\lambda_{\max}T=0.29 \text{ cm.} \times \text{deg}$. The energy in a quantum of light of this wave-length is given by

$$\epsilon = \frac{hV}{\lambda_{\max}} = 7 \times 10^{-16}T,$$

so that the quantum of light of any colour contains as much energy as nearly two atoms of the solid at the temperature at which light of this colour is emitted.

Thus it appears that the quantum is by no means a small amount of energy when compared with atomic energies.

30. Of the M vibrations, whether of material resonators or of light, considered in § 20, N were supposed to possess no energy at all. Thus, out of the whole number, only a fraction $\frac{M-N}{M}$ possess any energy, and the value of this fraction, by equation (29), is $e^{-2h\epsilon}$ or $e^{-\epsilon/RT}$. If ϵ/RT is large, only a small fraction of the vibrations will possess any energy; the majority will be perfectly at rest.

For instance, at 0°C ., $RT=3.6 \times 10^{-14}$ ergs, and the quantum for yellow light is 3.3×10^{-12} ergs, so that $\epsilon/RT=\text{about } 90$, and $e^{-\epsilon/RT}=\text{about } 10^{-39}$. If we suppose that each atom in a mass of sodium at 0°C . has associated with it a vibration of frequency equal to that of the D lines, then only one out of every 10^{39} of these vibrations will have any energy. Only one atom in 5×10^{10} tons of sodium will have any D-line energy to give out when in its steady state at 0°C .

Corresponding to the wave-length $\lambda_{\text{max.}}$, the value of the quantum is given by $\epsilon=4.965 RT$, so that even as regards light of wave-length $\lambda_{\text{max.}}$ at any temperature only one in $e^{4.965}$, or about 1 in 140, of the vibrations has any energy. Thus, in a red-hot mass of iron, less than 1 per cent. of the red vibrations have any energy: the remaining 99 per cent. are perfectly dead.

CHAPTER IV.

THE LINE SPECTRA OF THE ELEMENTS.

31. In the last two chapters it has been seen that mathematical analysis leads to the following quite definite results: (i.) The final steady state of any system in which the laws of Newtonian dynamics are obeyed must be one in which the partition of energy in the ether is given by the formula

$$8\pi RT\lambda^{-4}d\lambda \dots\dots\dots (42)$$

(ii.) To obtain a final steady state in which the partition of energy is given by Planck's law, and so agrees with observation, the motion of the system must be governed by the laws of the quantum-theory.

The laws of the quantum-theory have so far been obtained only in the mathematical form $\epsilon=h\nu$, with the restriction that exchanges of energy equal to fractions of the quantum ϵ cannot occur. These laws do not amount to a complete system of dynamical laws; indeed, it could hardly be expected that the complete system of laws governing the ultimate processes of Nature could be obtained from a study of the one phenomenon of black-body radiation. The laws, in so far as we have been able to obtain them, give no information as to motion which is not of a vibratory nature; they give no information as to any vibrations except perfectly isochronous ones; they require that exchanges of energy should take place by multiples of the quantum ϵ , but give no information as to when or why these exchanges of energy may be expected to take place. Finally, they give no indication at all as to the seat of these quanta of energy, whether they are to be looked for in the ether or in matter. The phenomenon of black-body radiation has yielded what information there is to be extracted from it; to complete our knowledge we must survey other phenomena of Nature. Incidentally, the discovery that other phenomena require laws similar to those of the quantum-theory will help to confirm the results obtained from the study of black-body radiation.

So far as concerns the problem of black-body radiation, the formula derived from the Newtonian laws was found to give a good approximation to the truth so long as x is small, where

$$x = \frac{h\nu}{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

Thus, perhaps, what is to be hoped from the quantum-theory is not so much that it shall annihilate our belief in the Newtonian laws as that it shall extend and amplify these laws so as to cover large values of x in the radiation problem, and correspondingly in other problems. (Compare, however, Poincaré's remarks given in § 24 of the last chapter.)

The physical meaning of the smallness of x , as given by equation (43), must first be considered. The numerator of x is $h\nu$, the quantum of energy; the denominator is RT , which is the mean energy of a vibration of great wave-length, and would be the mean energy of all vibrations if the Newtonian laws held. When this quantity RT contains many quanta, x is small; when it contains few quanta x is large. The Newtonian laws begin to fail as soon as the average energy RT does not contain a great number of quanta.

Many similar cases of apparent failures of laws in physics at once suggest themselves. The laws of gases begin to fail when the gas does not contain a great number of molecules, the laws of electricity fail when the charges or currents do not contain a great number of electrons, and so on. The laws which appear to fail are applicable to large-scale phenomena only; they take no account of the atomic nature of some entity, and so fail when applied to small-scale phenomena. Boyle's law is, so to speak, too coarse-grained to apply to single molecules, Ohm's law is too coarse-grained to apply to a few electrons. In the same way the Newtonian laws are too coarse-grained to apply to one or a few quanta.

The Newtonian laws apply, as an approximation, to the radiation problem when x is small—*i.e.*, when T is very large or when ν is very small. When T is very large, energy is very abundant; there are a great many quanta involved, and the atomicity of the quanta is of no account. When ν is very small, the quanta ($h\nu$) are very small, and again the atomicity is of no account.

The atomicity involved is not necessarily an atomicity of energy. RT is average energy, $1/\nu$ is the time of a vibration, so

that RT/ν is a physical quantity of dimensions (energy) \times (time). A quantity of these physical dimensions is spoken of as action. Thus, the Newtonian laws hold when the action RT/ν is great compared with the action h , of which the amount is known experimentally to be $h = 6.6 \times 10^{-27}$ ergs \times seconds. An alternative way of looking at the matter would be to suppose that "action" is atomic, that there is a universal atom of action of amount h , that the Newtonian laws take no account of this atomicity of action, and so are only valid approximations when the amount of action involved is a very great multiple of h . This way of regarding the situation is not limited to problems dealing with isochronous vibrations.

In searching for other phenomena in which the Newtonian laws break down it is natural to examine closely those in which the temperature is very low, or the frequency of a vibration very high, or the "action" of a process very small. In point of fact, each of these alternatives is found to lead to one phenomenon of importance in connection with the quantum-theory, these being respectively the phenomena of specific heats at low temperatures, of the line spectra of the elements, and of the photo-electric effect. Purely for convenience of arrangement, we may take the line-spectra first.

The Problem of the Line Spectra of the Elements.

32. So long as physicists thought in terms of the Newtonian mechanics almost every characteristic of the line-spectrum was a source of difficulty. The evidence both of emission and absorption suggested that the spectrum gave indication of either oscillations about a state of steady motion or vibrations about a state of rest of the dynamical system forming the atom. The discovery of the Zeeman effect and the explanation of it given by Lorentz in terms of the electron theory seemed to confirm these conjectures, and supplied the further information that the moving charges which were the origin of the emitted light were the moving electrons.

The first serious difficulty in this view was one which presented itself to Maxwell and Lord Kelvin. Each spectral line represented a separate vibration of the atom, and each vibration ought, according to the theorem of equipartition of energy, to have energy equal to RT . Thus a gas with n lines in its spectrum ought to have energy nRT per atom from its spectral vibrations alone. But the total energy of mercury is only

$\frac{3}{2}RT$ per atom, which is fully accounted for by the kinetic energy of motion of the atoms; the total energy of hydrogen is only $\frac{5}{2}RT$ per molecule and so on.

A further difficulty arose in connection with the number of moving electrons per atom. For, if the atom were a system of vibrating or oscillating electrons, there ought to be a number of spectral lines not greater than three (at most) times the number of electrons. But various lines of evidence have for some time combined in indicating that the number of optically-active electrons in an atom was at most of the order of magnitude of the atomic weight. It was clearly impossible to account for the complicated spectra of hydrogen and helium in this way.

Finally, it was found that the frequencies of the spectral lines fall into the well-known spectral series, which could not be interpreted on the older mechanics; indeed the mere circumstance that the atom gave sharply defined lines at all was sufficiently difficult of interpretation. The following quotations from a Paper by Lord Rayleigh* will indicate the nature of some of the difficulties encountered:—

“In the calculation of frequencies for a cloud of electrons the undisturbed condition is one of equilibrium, and the frequencies of radiation are those of vibration about this condition of equilibrium. Almost every theory of this kind is open to the objection that I put forward some years ago (‘Phil. Mag.’ 1897, 44, p. 362; ‘Scientific Papers,’ IV., p. 345), viz., that p^2 and not p is given in the first instance. It is difficult to explain on this basis the simple expressions found for p , and the constant differences manifested in the formulæ of Rydberg and of Kayser and Runge. . . .

“In recent years theories of atomic structure have found favour, in which the electrons are regarded as describing orbits, probably with great rapidity. If the electrons are sufficiently numerous there may be an approach to steady motion. In case of disturbance oscillations about this steady motion may ensue, and these oscillations are regarded as the origin of luminous waves of the same frequency. But, in view of the discrete character of electrons, such a motion can never be fully steady, and the system must tend to radiate even when undisturbed (*cf.* Larmor, ‘Matter and Æther’). . . .

“An apparently formidable difficulty . . . stands in the

* “Phil. Mag.,” January, 1906.

way of all theories of this character. How can the atom have the definiteness which the spectroscope demands? It would seem that variations must exist in (say) hydrogen atoms which would be fatal to the sharpness of the observed radiation; and, indeed, the gradual change of an atom is directly contemplated in view of the phenomenon of radioactivity."

In brief, as the atom radiates, its total energy changes, so that the orbits of its electrons change, and consequently the frequencies of the oscillations about these orbits change. Each atom in a gas would thus have its own spectrum, so that the spectroscope ought, on this view, to show continuous radiation and not sharp lines.

33. Since Lord Rayleigh wrote the Paper (1906) from which the foregoing quotations have been taken, our knowledge of atomic structure has progressed from speculation to something approaching fairly near to certainty. There seems to be little room for doubt now that the atom is built after what may be called the Rutherford* model, according to which the atom consists of a central nucleus of dimensions that may be regarded as infinitesimal, and of electrons revolving in planetary manner around this nucleus.

The argument for this type of atom may, perhaps, conveniently start from a consideration of the helium atom. The α -ray particle has been shown to be a helium atom with a positive charge equal to exactly twice the electronic charge—in other words, the α -particle is a helium atom from which two electrons have been removed, or, again, the normal helium atom consists of an α -ray particle and two electrons. The extraordinary penetrating power of the α -particle shows that it must be something extremely small and compact—of size, perhaps, something less than 10^{-12} cms. and of compactness such that nothing seems to affect its structure. This is the nucleus of the helium atom; ordinary methods of gas theory indicate that the size of the complete atom is of the order of 10^{-8} cms., which gives information as to the size of the orbits described by the two electrons around the nucleus. The nucleus possesses practically all the mass of the atom, and so may be regarded as a massive fixed point around which the comparatively weightless electrons move.

There is strong evidence that this structure is not a peculiarity of the helium atom, except as regards the special number

* "Phil. Mag.," 21 (1911), p. 669, and 27 (1914), p. 488.

of electrons (two) involved. According to the experiments of Geiger and Marsden* and the calculations of Rutherford† and Darwin‡, the scattering of both α and β -particles by every kind of matter examined was exactly what was to be expected if matter of all kinds had the structure suggested by Rutherford. A great deal of work has naturally been expended on the determination of the numbers of electrons in the different elements. It now seems highly probable§ that the number of positive unit charges contained in the nucleus is equal to what is called the atomic number, which, in turn, is the number identifying the position of the element when all elements are arranged in order beginning with the lightest. Calling their number N , we have for hydrogen $N=1$, for helium $N=2$ (as has already been seen), and so on.

Thus, according to this view, which is supported by a much greater volume of evidence than can be referred to here, the hydrogen atom consists of a negative electron revolving in an orbit round a positive nucleus of equal charge, while the helium atom consists of two electrons revolving in orbits round a nucleus with a positive charge equal in amount to twice that of an electron.

The inability of the Newtonian mechanics to explain line spectra becomes evident if we fix our attention on the hydrogen atom, which consists of two point charges only, one positive and one negative, and yet gives the highly complicated spectrum associated with hydrogen. We are at once led to inquire why these two charges continue rotating round one another, instead of falling into one another, as the energy of their motion is dissipated by radiation. And how can such a simple system give a spectrum containing so many lines? The number of degrees of the system is only six, three of which represent its ability to move in space. How, then, can so many vibrations be possible? And, again, why does not the energy of these vibrations appear in the measure of the specific heats? To all these questions the Newtonian mechanics can give no answer. The answer given by the quantum-theory is, perhaps, only partial, but, as we shall see, it is so convincing that little doubt can be felt of its fundamental accuracy.

* "Proc." Roy. Soc., A. 82, p. 495 (1909), and later Papers.

† "Phil. Mag.," 21 (1911), p. 669.

‡ "Phil. Mag.," 25 (1913), p. 201, and 23 (1912), p. 901.

§ H. G. J. Moseley, "Phil. Mag." 26 (1913), p. 1024, and 27 (1914), p. 703.

Nicholson's Theories of the Line-Spectrum.

34. The first serious progress made towards the interpretation of the line-spectrum is due to J. W. Nicholson.* Nicholson studied in particular the spectrum which was to be expected from atoms built on the Rutherford model, and having four and five positive unit charges respectively in the nucleus. The former of these elements he called *nebulium*, and the latter *protofluorine*. These names were allotted in the belief, then held by Nicholson, that they were primitive forms of matter, more fundamental than hydrogen, the former being observable in the nebular, and the latter in the coronal, spectrum. The electrons were in each case supposed to move in steady motion in a circular ring about the nucleus, and the possible oscillations about this state of steady motion were first calculated by the Newtonian mechanics. The possible oscillations fall, as can easily be seen, into two quite distinct classes—oscillations normal to the plane of the ring, in which each electron keeps its distance from the nucleus unaltered, and oscillations in the plane of the ring. There is, of course, nothing in the assumed structure of the atom to fix the radius of the ring of electrons: this depends on the energy of the atom, and so ought continually to change as the atom loses energy by radiation. But for an assumed radius a the frequencies of the oscillations can be calculated, and vice versa, and certain ratios of frequencies of oscillations will not depend on a .

Nicholson calculates the frequencies of the oscillations normal to the plane and certain of their ratios which do not involve a . It is found to be possible to pick out pairs of lines in the observed spectra of *nebulæ* or the *corona*, as the case may be, having exactly the calculated ratio of frequencies; the number of such ratios for which the observed and calculated values are in almost exact agreement is believed by Nicholson to put any explanation in terms of the theory of coincidences out of court entirely. From any such pair of lines, when it has been found, it is, of course, possible to calculate a , the radius of the ring of electrons. The radius of the ring is not however, found to have always the same value when determined from different pairs of lines.

Nicholson also calculates the frequencies of the oscillations in the plane. Many of these oscillations are found to be *unstable*.

* Nicholson's Papers will be found in the Monthly Notices of the Royal Astr. Soc. from 1912 to 1914.

Thus the ring of electrons, according to the Newtonian mechanics, could not continue for any length of time in existence as a ring; the slightest jar which it might receive would cause it either to explode or collapse. Consequently the oscillations normal to the plane of the ring can only have a real existence if it is supposed that in some way the oscillations in the plane of the ring are either prevented from taking place altogether or are governed by some system of dynamics different from the Newtonian system. The sharpness of the observed spectral lines demands that the radius of the ring of electrons should remain invariable, or should have only a definite number of possible values, jumping from one to the other instantaneously, perhaps, as the energy is lost by radiation. Whatever view is taken it is obvious that something quite different from the Newtonian mechanics will be required to explain the motion. Nicholson believes he can find quite distinct evidence of the existence of Planck's quantum from a study of the radii of the different rings, but his work is hardly complete enough yet to admit of abstraction as a finished theory. We may take leave of it with the remark that, in addition to whatever it may achieve when more fully developed, it has probably already succeeded in paving the way for the ultimate explanation of the phenomenon of the line spectrum.

Bohr's Theories of the Line Spectrum.

35. In July, 1913, there appeared the first of a series of very remarkable and intensely interesting Papers by Dr. Bohr, of Copenhagen,* in which he explains how the Rutherford conception of the atom together with a system of mechanics based on the quantum-theory can be made to yield an explanation of the series observed in the line spectra of hydrogen, and of other phenomena. The theory advanced by Dr. Bohr explains so many facts, and its numerical agreement with observation is so complete, that little doubt will be felt that it is at least based on a very substantial substratum of truth.

Bohr considers first the simplest case of a Rutherford atom, in which a single electron of mass m and charge $-e$ is supposed to describe an orbit of radius a round a nucleus of charge E and of mass M so large that the nucleus may be supposed to remain at rest, at any rate for preliminary approximate calculations.

* "Phil. Mag.," 26 (1913), p. 1, and 476, and later Papers, also in the "Phil. Mag."

Bohr takes ω to be the frequency of revolution of the electron in its orbit, so that $2\pi\omega$ is the angular velocity with which this orbit is described. Then, according to the Newtonian mechanics, the condition that a circular orbit of radius a may be possible is

$$\frac{eE}{a^2} = (2\pi\omega)^2 ma. \quad . \quad . \quad . \quad . \quad . \quad (44)$$

The kinetic energy of the electron is $\frac{1}{2}m(2\pi\omega a)^2$, or $\frac{1}{2}\frac{eE}{a}$. The work required to move the electron from its orbit to a position of rest at infinity is $\frac{eE}{a} - \frac{1}{2}m(2\pi\omega a)^2$, or again $\frac{1}{2}\frac{eE}{a}$. Denoting this quantity, the negative energy of the orbit, by W , it is readily found that

$$2a = \frac{eE}{W}; \quad \omega = \frac{\sqrt{2}}{\pi} \frac{W^{\frac{3}{2}}}{eE\sqrt{m}}. \quad . \quad . \quad . \quad . \quad (45)$$

These equations have been obtained by the Newtonian mechanics. Now, according to the Newtonian mechanics the loss of energy W ought to go on increasing as energy was dissipated by radiation, so that a would continually decrease and ω increase. The orbit would get smaller and more rapid until the electron fell into the nucleus, and as this process was going on any spectrum emitted by the system would naturally undergo continual change. These considerations illustrate in a forcible way the inability of the old mechanics to account for the line spectrum.

36. Bohr introduces, to avoid all these difficulties, an assumption which is not inconsistent with the quantum-theory and is closely related to it. It has been noticed already that the quantum-theory is not in itself a complete system of dynamics, and so must not be expected to give a full account of phenomena by itself. The complete system of dynamics, of which it is a part, has not yet been found, and Bohr's assumption only amounts to adding tentatively one other brick to the foundation already laid by Planck's equation $\varepsilon = h\nu$.

Bohr's assumption, introduced at present only with reference to the atom with one electron, is contained in the equation

$$W = \tau h \frac{\omega}{2}, \quad . \quad . \quad . \quad . \quad . \quad (46)$$

in which h is Planck's constant and τ is an integer. Various

physical interpretations can be given to this equation. Perhaps the simplest is the following: The angular momentum of the electron in its orbit is $2\pi m\omega a^2$ or $W/\pi\omega$. Bohr's assumption, expressed in equation (46), makes this equal to $\tau h/2\pi$, i.e., to an integral multiple of the universal constant $h/2\pi$, and so is equivalent to assuming that angular momentum is atomic, and that $h/2\pi$ is the unit. An alternative physical interpretation is suggested by Bohr, and will be found in his Paper (p. 4, last para.).

The effect of Bohr's assumption is, of course, to prevent the continuous variations of W , a and ω , which would be demanded by the Newtonian mechanics. The values of W , a and ω are found, from equations (45) and (46), to be

$$W = \frac{2\pi^2 m e^2 E^2}{\tau^2 h^2}, \quad 2a = \frac{\tau^2 h^2}{2\pi^2 m e E}, \quad \omega = \frac{4\pi^2 m e^2 E^2}{\tau^3 h^3}. \quad (47)$$

Instead of τ varying continuously, as it would in the older mechanics, it is now restricted to integral values. How complete a difference there is between the two systems will be realised on considering the variations of angular momentum demanded in the two cases. According to the classical mechanics, the electron experiences a retarding force, F , equal to $\frac{2}{3} \frac{e^2}{V^3} (2\pi a \ddot{\omega})$ from its interaction with the ether, and the rate of loss of its angular momentum $\tau h/2\pi$ is given by

$$\frac{d}{dt} \left(\frac{\tau h}{2\pi} \right) = -F,$$

while, according to the new hypotheses of Bohr, $d\tau/dt$ has no meaning at all! The effect of restricting τ to integral values is, of course, to limit W , ω and a to certain definite values. For instance, a cannot gradually shrink, but the electron is limited to one of the values of a given by

$$a = \frac{\tau^2 h^2}{4\pi^2 m e E},$$

where $\tau^2 = 1, 4, 9, 16, 25, \dots$

Since a cannot undergo slight changes, there can be no oscillations in the plane of the orbit, and the circumstance discovered by Nicholson, that such oscillations would, on the old mechanics, be unstable, is no longer an objection. The normal hydrogen atom will be that in which the loss of energy has been greatest, and so is given by $\tau = 1$. On putting in

numerical values, the diameter of the orbit is found to be given by $2a=1.1 \times 10^{-8}$ cm., which is certainly of the right order of magnitude. But it is an essential part of Bohr's theory that there can be hydrogen atoms of sizes 4, 9, 16, 25, . . . times this.

37. The radius of the electron orbit of a particular atom is not supposed to be fixed for all time, and we have to consider the possibility of a sudden shrinkage from, say, the orbit given by $\tau=\tau_1$ to the orbit given by $\tau=\tau_2$. No suggestion is made by Bohr's theory as to what determines when this shrinkage shall take place, or how it happens, but the formulæ already obtained show that when it does happen the system must experience a loss of energy of amount δW given by

$$\delta W = W_{\tau_2} - W_{\tau_1} = \frac{2\pi^2 m e^2 E^2}{h^2} \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right). \quad (48)$$

Bohr supposes that the whole of this energy, suddenly set free from the atom, passes away into space in the form of absolutely monochromatic radiation. He further supposes that *the amount of this radiation is exactly one quantum*. Thus δW , given by equation (48), must be the same as ε in Planck's equation, and therefore equal to $h\nu$. This condition, according to Bohr, determines the frequency of the monochromatic light emitted. Putting the right-hand of equation (48) equal to $h\nu$, the frequency is seen to be given by

$$\nu = N \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right), \quad (49)$$

where

$$N = \frac{2\pi^2 m e^2 E^2}{h^3}. \quad (50)$$

According to Bohr's theory, the different values of τ_1 and τ_2 which can be inserted in this equation must give the frequencies of the different spectral lines of the substance. The lines can be sorted into series corresponding to different values of τ_2 . For instance, there will be a series given by $\tau_2=1$, and the lines of this series will be given by $\tau_1=2, 3, 4, \dots$; there will be a series $\tau_2=2$, with lines given by $\tau_1=3, 4, 5, \dots$; and so on.

38. *Hydrogen Spectrum.* To obtain the hydrogen spectrum, we simply take $E=e$, and so

$$N = \frac{2\pi^2 m e^4}{h^3}. \quad (51)$$

The series $\tau_2=2$ gives the series of lines

$$\nu = N \left(\frac{1}{4} - \frac{1}{n^2} \right),$$

where n has the values 3, 4, 5, ..., and this is exactly the well-known Balmer's series. The numerical agreement is almost perfect, for on substituting the best known values for m , e and \hbar , the calculated value of N is 3.26×10^{15} , whereas the observed value is 3.290×10^{15} , the error thus being well within the probable errors in the assumed values of e and \hbar .

The value $\tau_2=1$ in equation (49) would give the series

$$\nu = N \left(1 - \frac{1}{n^2} \right), \quad (n=2, 3, 4, \dots),$$

all the lines of which would be in the extreme ultra-violet. None of the lines of this series had been observed when Bohr published his Paper, but the series has since been discovered by Lyman.*

The value $\tau_2=3$ gives the series

$$\nu = N \left(\frac{1}{9} - \frac{1}{n^2} \right), \quad (n=3, 4, 5, \dots),$$

which is exactly the series observed by Paschen† in the infra-red. The series $\tau_2=4, 5, 6, \dots$ are too far in the infra-red to be observed.

This completes the list of lines obtainable from formula (49), and it will be noticed that certain lines, usually ascribed to hydrogen, have not been accounted for. Bohr shows that many of these missing lines are readily explained as belonging to helium.

39. *Helium Spectrum*.—For helium the nuclear charge E is $2e$, and in the neutral helium atom there are two electrons describing orbits. A helium atom with one positive charge will, however, have only one electron describing an orbit around a charge $2e$, so that the spectrum of such an atom ought to be obtained on putting $E=2e$ in equation (49). If we keep for N the value assigned to it in equation (51), this spectrum can be put in the form

$$\nu = 4N \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right) = N \left(\frac{1}{\left(\frac{\tau_2}{2}\right)^2} - \frac{1}{\left(\frac{\tau_1}{2}\right)^2} \right). \quad \dots \quad (52)$$

The series $\tau_2=1$ and $\tau_2=2$ lie in the extreme ultra-violet, and

* Details have not yet been published.

† "Annalen der Physik," 27 (1908), p. 565.

have not been observed. The series $\tau_2=3$ may be regarded as falling into two parts according as τ_1 is odd or even, namely

$$\nu=N\left(\frac{4}{9}-\frac{1}{n^2}\right), \quad \nu=N\left(\frac{4}{9}-\frac{1}{(n+\frac{1}{2})^2}\right),$$

and these are two of the series recently observed by Fowler* in a mixture of hydrogen and helium. These series were at first attributed by Fowler to hydrogen, although from the first it was apparent that they could not be obtained without an admixture of helium. In view of Bohr's explanation it now seems reasonable to attribute them to positively charged helium atoms, the hydrogen presumably being necessary to effect the ionisation of the helium.

The series $\tau_2=4$ may again be regarded as falling into two parts, according as τ_1 is odd or even, namely—

$$\nu=N\left(\frac{1}{4}-\frac{1}{n^2}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

$$\nu=N\left(\frac{1}{4}-\frac{1}{(n+\frac{1}{2})^2}\right). \quad . \quad . \quad . \quad . \quad . \quad (54)$$

The first of these is obviously Balmer's series, so that the lines of this series can be emitted by helium as well as by hydrogen. The second is the series observed by Pickering in the star ζ -Puppis in 1896.† This series was attributed by Pickering to hydrogen simply from the analogy, now seen to be inadequate, that the series (53) was emitted by hydrogen. In the ζ -Puppis spectrum, in point of fact, the series (53) is observed to be more intense than the series (54), presumably indicating that the source of light is a mixture of hydrogen and helium.

40. One point of interest arises in connection with these stellar spectra. In the laboratory it is not possible to observe the Balmer series beyond the line $n=12$, while in the stellar spectra this series appears as far as $n=33$. The inference, on Bohr's theory, is that in the vacuum-tubes available in the laboratory there are no hydrogen atoms of diameter greater than that given by $\tau_1=12$, whereas in the stars there are atoms of diameter up to that given by $\tau_1=33$. For $\tau=12$ the calculated diameter is 1.6×10^{-6} cms., which is equal to the mean distance between the molecules in a gas at a pressure of about

* Monthly Notices Royal Ast. Soc., 73, December, 1912.

† "Astrophysical Journal," 4 (1896), p. 369, and 5 (1897), p. 92.

7 mm. of mercury ; for $\tau=33$, the corresponding diameter is 1.2×10^{-5} cms., and the pressure about 0.02 mm. of mercury. Thus, Bohr's theory leads us to suppose that in the stars there may be hydrogen atoms of diameter about one thousand times that of the normal atom.

41. The brief calculations given above have proceeded on the supposition that the mass of the nucleus M is very great compared with that of the electron m . If this assumption is no longer retained, the value of N , the Rydberg's constant for the various series, instead of being given by equation (50), is found to be given by*

$$N = \frac{2\pi^2 e^2 E^2}{h^3} \frac{mM}{(M+m)} \cdot \cdot \cdot \cdot \cdot \quad (55)$$

Thus, if M refers to the hydrogen nucleus, the mass of the helium nucleus will be $4M$, and instead of the ratio of the two N 's being, as was given by the simple approximate calculations, 4 to 1, it will be

$$\frac{4}{M + \frac{1}{2}m} : \frac{1}{M+m}.$$

From the observed ratio of the two N 's, taken from the best measurements of the hydrogen and helium lines, Fowler † obtains for the ratio M/m the value 1,836, with a probable error of not more than 12. It need hardly be said in what good agreement this value is with other determinations of M/m .

42. The foregoing remarks refer only to Bohr's interpretation of the hydrogen and helium spectra. One other case in which his theory seems to be successful is that of the single electron rotating round a nucleus of charge $3e$. This atom, on Bohr's view, is the lithium atom with a double positive charge, and it ought to show spectral lines of frequencies

$$\nu = 9N \left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2} \right).$$

The special value $\tau_1=6$ gives, in addition to lines coinciding with those of the Balmer series, a pair of series

$$\nu = N \left(\frac{1}{4} - \frac{1}{(m \pm \frac{1}{3})^2} \right), \cdot \cdot \cdot \cdot \cdot \quad (56)$$

some of the lines of which have been identified by Nicholson ‡ in the spectra of the Wolf-Rayet stars.

* Bohr, "Phil. Mag.," March, 1914, p. 509.

† Royal Society, Bakerian Lecture, 1914.

‡ Monthly Notices of the Royal Ast. Soc., March, 1913, p. 382.

43. This brief summary of Dr. Bohr's work has only attempted to touch on a few of the very interesting points covered by his original Papers. Enough has, however, perhaps been said to indicate how rich a field is opened by the application of the quantum-theory to problems of atomic structure.

It will be seen, on examination of Bohr's work, that its most marked successes occur in the case of a single electron rotating round a nucleus ; indeed, in more complex cases, the success of Bohr's theory is at least open to doubt. It almost would appear as though the motion of the simple system consisting of a nucleus and one electron was governed by the laws assumed by Bohr, while the mechanics of the more complex system consisting of more than two parts had not been fathomed yet.*

One general reflection may perhaps be made about the general problem of the line spectrum. One of the most noticeable features of the general system of line spectra is the way in which the well-known Rydberg constant enters similarly into the spectra of all substances. The natural interpretation of this would be to suppose that this constant depended only on quantities common to all kinds of matter, or, more mathematically, to suppose that the constant was a function only of e , m and V , the velocity of light. But it is at once found that no constant of the same physical dimensions as Rydberg's constant can be constructed out of the quantities e , m and V . The quantum-theory, however, puts the additional quantity h at our disposal. As we have seen, it is now possible to construct the Rydberg constant as a function of e , m , V and h . The constant so constructed has exactly the right numerical value, and even its slight variations can perhaps (*cf.* § 41) be accounted for by the different values of m/M for the different elements. The point which is worth considering is briefly this: The existence of Rydberg's constant indicated that there must be some universal constant common to all matter in addition to the previously known constants e , m and V , and the constant h of the quantum-theory has been found to supply the omission exactly.

* See a Paper by J. W. Nicholson, Monthly Notices of the Royal Ast Soc., March, 1914, p. 425.

CHAPTER V.

THE PHOTO-ELECTRIC EFFECT.

44. No single feature of the quantum-theory causes more difficulty in its acceptance than the postulate that radiant energy must, so to speak, be in some way tied up in bundles of amount $h\nu$. Whether this postulate is absolutely essential to the quantum-theory will, in the present report, be discussed in a later chapter, after all the evidence has been reviewed. The view that radiant energy exists in the form of indivisible "light-quanta" has been put forward and defended by Einstein,* and has been the centre of much discussion. The photo-electric phenomenon, which will be discussed in the present chapter, is of special interest, as throwing light on this important question, as well as giving evidence as to the validity of the general theory of quanta.

The general features of the phenomenon are well-known.† For some time it has been known that the incidence of high-frequency light on to the surface of a negatively charged conductor tended to precipitate a discharge, while Hertz showed that the incidence of the light on an uncharged conductor resulted in its acquiring a positive charge. These phenomena have been shown quite conclusively to depend on the emission of electrons from the surface of the metal, the electrons being set free in some way by the incidence of the light.

In any particular experiment, the velocities with which individual electrons leave the metal have all values from zero up to a certain maximum velocity v , which depends on the conditions of the particular experiment. No electron is found to leave the metal with a velocity greater than this maxi-

* "Ann. der Physik," 17 (1905), p. 132, 20 (1906), p. 199, 22 (1907), 180. See also various letters in the "Physikalische Zeitschrift," and §§ 64, 65 of the present report.

† A very good summary will be found in Campbell's "Modern Electrical Theory" (2nd edition, 1913), while a more complete account is given by Hughes, "Photo-Electricity" (Camb. Univ. Press, 1914). I have drawn freely from both of these sources in writing the present chapter. See also Richardson and Compton, "Phil. Mag.," 24 (1912), p. 575, and Hughes, "Phil. Trans. Roy. Soc.," 212, A (1912), p. 205.

imum v . It seems probable that in any one experiment all the electrons are initially shot off with the same velocity v , but that those which come from a small distance below the surface lose part of their velocity in fighting their way out to the surface.

Leaving out of account such disturbing influences as films of impurities on the metallic surface, it appears to be a general law that the maximum velocity v depends only on the nature of the metal and on the *frequency* of the incident light. It does not depend on the *intensity* of the light, and within the range of temperature within which experiments are possible it does not depend on the temperature of the metal. The non-dependence on intensity was first established by Lenard,* and has subsequently been confirmed in an interesting way by Pohl and Pringsheim† and by Millikan,‡ who found that the maximum velocity was the same whether using either very intense spark-light, or are light of the same wave length. And, as regards dependence on temperature, Ladenburg§ has examined the photoelectric effect for three metals (Au, Pt and Ir) up to 800°C., and found it independent of the temperature, while Lienhop§ has worked down to -180°C. with the same result.

For a given metal this maximum velocity increases regularly as the frequency of the light is increased, but there is a certain frequency below which no emission takes place at all. There is almost general agreement now that if v is the maximum velocity for light of frequency ν falling on a given metal, the kinetic energy $\frac{1}{2}mv^2$ is given by

$$\frac{1}{2}mv^2 = h\nu - w_0, \quad . \quad . \quad . \quad . \quad . \quad (57)$$

where h , w_0 are constants for the metal. The frequency ν_0 , below which no emission takes place, is, of course, given by $\nu_0 = w_0/h$. As an instance may be taken its value for sodium, for which $\nu_0 = 5.15 \times 10^{14}$, which is the frequency for green light. Light more red than this can fall on sodium for centuries without producing any photo-electric effect at all; the incidence of light more violet than this will immediately result in an emission of electrons with a maximum kinetic energy $h(\nu - \nu_0)$.

* "Ann. d. Phys.," 8 (1902), p. 149.

† "Verh. d. Deutsch. Phys. Gesell.," 15 (1912), p. 974.

‡ "Verh. d. Deutsch. Phys. Gesell.," 9 (1907), p. 165.

§ "Ann. d. Phys.," 21 (1906), p. 281.

45. As a typical set of good experimental determinations may be taken those of Hughes.* The quantity w_0 , being of the physical dimensions of energy, may be put equal to eV_0 , where V_0 is the P.D. through which an electron would have to fall to acquire kinetic energy w_0 . The values obtained by Hughes for k and V_0 are given in the following table (the last column but one is different from that actually printed in Hughes' Paper, because he uses k in a different sense) :—

| Element. | Atomic weight. | Atomic volume. | Valency. | k . | V_0 (volts). |
|----------------------|----------------|----------------|----------|------------------------|----------------|
| Ca | 40.1 | 25.4 | 2 | 4.91×10^{-27} | 2.57 |
| Mg | 24.3 | 14.0 | 2 | 5.24 | 3.08 |
| Cd | 112.4 | 13.0 | 2 | 5.67 | 3.49 |
| Zn | 65.4 | 9.2 | 2 | 5.88 | 3.77 |
| Pb | 207.1 | 18.1 | 4 | 5.50 | 3.42 |
| Bi | 208.0 | 21.2 | 5 | 5.63 | 3.37 |
| Sb | 120.2 | 18.1 | 5 | 5.72 | 3.60 |
| As | 75.0 | 13.1 | 5 | 5.7 | 4.5 |
| Se | 79.2 | 17.6 | 6 | ... | 4.8 |
| O ₂ | 16.0 | 12.6 | 6 | ... | 8.0 |

Hughes points out that in any set of elements of the same valency there is a regular increase in k and V_0 with decreasing atomic volume, and that in passing from one valency to another this relation is discontinuous, the discontinuity being always in the same direction. It will be noticed that V_0 is certainly of the same order of magnitude as the ionisation potential, and may probably with fair certainty be identified with it. For oxygen Hughes finds $V_0=8.0$ volts, while the best direct determination of the ionisation potential gives 8.1 volts.†

46. If we assume this identification, w_0 in equation (57) becomes identical with the amount of energy required to move the electron out of its atom to rest at a point outside the attraction of the atom. The amount of work needed to move the electron away from its atom and endow it with a velocity v is $\frac{1}{2}mv^2 + w_0$, and this, by equation (57), is equal to $h\nu$.

Now the average value of k for the elements examined by Hughes is about 5.5×10^{-27} , while Planck's constant h is 6.6×10^{-27} . Thus the amount of energy $h\nu$ absorbed by the electron in setting itself free from the atom is always nearly equal to one quantum of energy, irrespective of the frequency

* "Phil. Trans.," 212, A (1912), p. 225.

† Hughes, *l.c.*, p. 223.

of the incident light. The whole phenomenon is very clearly and adequately explained on the quantum-theory, if we suppose that the total energy absorbed by the atom and electron together is exactly one quantum, and that about five-sixths of this is absorbed by the electron, while the remaining one-sixth is absorbed by the remainder of the atom. A general explanation of the photo-electric phenomenon in terms of the quantum-theory was first put forward by Einstein.*

This explanation of the photo-electric effect seems to demand that energy of frequency ν should exist in the ether in indivisible bundles of amount $h\nu$, or, at least, that interchanges of energy between matter and ether, at any rate so far as this special type of interchange is concerned, should occur by indivisible quanta of amount $h\nu$. On this view of the matter it is obvious why light of frequency less than the critical frequency $\nu_0 = w_0/k$ cannot produce any emission of electrons. For one quantum of such energy is not adequate to remove the electron from its orbit, and the chance of two quanta being incident on the atom simultaneously may be treated as negligible. Again, it is obvious why the speed of emission must increase with the frequency of the incident light; for the atom, if it absorbs energy from the ether at all, cannot absorb less than the whole of the quantum—the quantum being supposed indivisible—and so any excess of energy in the quantum over that required to remove the electron from its orbit must appear (mainly) as kinetic energy of the electron (equation (57)).

47. It cannot be denied that very serious difficulties can be formulated against Einstein's conception of the energy quantum (*cf.* below, § 65). Without stopping to discuss these difficulties now, we may inquire whether an alternative explanation, more on the lines of the older mechanics, cannot be given of the photo-electric phenomenon.

Those who attempt such an explanation have to fall back on some kind of "trigger action" and resonance effect.† For instance, the critical frequency for sodium is $\nu_0 = 5.15 \times 10^{14}$; light of frequency greater than this will liberate electrons, while light of lower frequency, no matter how intense, will produce no effect at all. This has to be explained by supposing that in a mass of sodium there are a number of atoms in which

* "Annalen der Physik," 17 (1905), p. 146.

† In particular, Lenard, "Ann. der Physik," 8 (1902), p. 149. See note on next page.

electrons are oscillating with frequencies, say, 5.2×10^{14} , 5.3×10^{14} , 5.4×10^{14} , and so on, and that the amplitudes of these vibrations are so great that each electron is just about to jump out of its orbit and free itself from its atom. If this were so, it can readily be imagined that a small amount of light of any frequency greater than 5.15×10^{14} would so increase the amplitude of vibration of those atoms with which it was approximately in resonance that they would soon escape altogether. But, to account for the fact that light of frequency less than ν_0 can produce no effect, it would have to be supposed that there were no such oscillations of frequencies 5.1×10^{14} , 5.0×10^{14} , and so on.

Even if all this could be accepted, it would only explain why photo-electric action could take place, and not at all why it should be governed by an equation of the form of (57). But the explanation is not in keeping with the teachings of the sodium spectrum as to the frequencies of the oscillations in the sodium atom, and even if it were, it would be difficult to understand why it is that, if very faint light of frequency 5.2×10^{14} can produce enough resonance for electrons to be set free, very intense light of frequency 5.1×10^{14} cannot produce the same effect. Moreover, the view that the sodium atoms have large stores of energy of internal vibration is not one which can be reconciled either with our knowledge derived from specific heats or spectroscopy.

48. If it is once granted that a "trigger action" of this type is inadmissible* there is a very convincing argument against any explanation in terms of the old undulatory theory of light. This is stated with great clearness by Campbell as follows † :—

"There is one remarkable feature connected with the photo-electric effect which shows that the older view is quite inadequate, and that some reconstruction of our ideas is necessary, while it is in complete agreement with Einstein's theory. A photo-electric effect can certainly be observed when the energy falling per second on 1 sq. cm. of the substance is much less than 1 erg (which is equivalent to a standard candle at a distance of 2 metres), and the energy of each electron liberated by it can certainly be greater than 10^{-12} ergs (corresponding to 0.6 volt). On the ordinary theory of light an electron cannot

* Lenard has recently agreed that the photo-electric energy must come from the incident light. See Ramsauer, "Physikalische Zeitschrift," 12 (1911), p. 997.

† "Modern Electrical Theory" (2nd edition, 1912), p. 249.

absorb more energy than falls on the molecule in which it is contained; but the area covered by the section of a single molecule is certainly less than 10^{-15} cms.* It appears, then, that no electron could acquire the energy with which it actually emerges unless the light had acted for 10^3 sec., or about a quarter of an hour; until this time has elapsed from the moment when the light was turned on, there should be no photo-electric effect. As a matter of fact, the effect appears to start absolutely simultaneously with the action of the light.

"But if the light energy is done up in bundles or quanta, and an electron can take up a whole quantum instantaneously, then there can be a photo-electric effect resulting in the emission of a single electron as soon as the *total energy* of the light emitted is equal to one quantum. Now the source contemplated is emitting light at the rate of 5,000 ergs a second, so that only 2×10^{-16} secs. need elapse before a quantum is emitted. This time is, of course, wholly inappreciable."

These considerations show very clearly the inability of the old undulatory theory to explain the photo-electric effect.

49. It is worthy of notice† that Einstein's theory, which has been seen to give such a satisfactory explanation of the photo-electric effect, falls into place very naturally as a logical extension of Bohr's theory, which in the last chapter was seen to account for the observed phenomena of line spectra. The quantity w_0 which has been used in this chapter is the amount of energy required to set the electron free, without velocity, from its orbit, and so is exactly equal to the quantity denoted by W in the last chapter. If we suppose W_1 to be the lost energy in the normal state, corresponding to $\tau=1$ in the last chapter, and W_∞ to be the lost energy in the state $\tau=\infty$, in which the electron is free at infinity, then $W_1=w_0$ and $W_\infty=0$. If, for simplicity in argument, we neglect the difference between h and k , i.e., if we assume that the whole quantum of energy is absorbed by the electron ultimately set free, then equation (57) becomes

$$\frac{1}{2}mv^2 = h\nu - w_0 = h\nu - (W_1 - W_\infty),$$

or
$$h\nu = W_1 - W_\infty + \frac{1}{2}mv^2. \quad . \quad . \quad . \quad . \quad . \quad (58)$$

* See Marx and Lichtenecker, Ann. d. Phys., 41 (1913), p. 124; also Marx, Ann. d. Phys., 41 (1913), p. 161.

† Bohr, "Phil. Mag.," 26 (1913), p. 17.

Bohr's equation giving the line spectrum was (*cf.* equation (48))

$$h\nu = W_{\tau} - W_{\tau_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

This equation referred to the *emission* of radiation accompanying the shrinkage of the atom from the state τ_1 to the state τ_2 . The physical process must, however, be reversible, so that the incidence of a quantum of energy of frequency ν given by equation (59) on an atom in the state τ_2 ought to result in the absorption of the radiation and the expansion of the atom to the state τ_1 . Thus a line of this frequency ought to appear in the absorption spectrum of the gas, provided there are atoms in the gas in the state τ_2 ; if there are no atoms in this state, there would be no absorption of light of this frequency. For instance, in ordinary inert hydrogen there are presumably no atoms in the state $\tau_2=2$, so that the corresponding lines, which constitute the Balmer series, do not appear as absorption lines. In general, when atoms occur in an inert gas, they may all be expected to be in the final state in which $\tau=1$, so that the only lines of the emission spectrum which may be looked for in the absorption spectrum will be the lines given by $\tau_2=1$, namely, lines of frequency given by

$$h\nu = W_1 - W_n \dots (n=2, 3, 4, \dots \infty). \quad . \quad . \quad . \quad (60)$$

If radiation of one of these frequencies falls on a gas it will be absorbed; if radiation of a frequency intermediate between these frequencies falls on a gas it will not be absorbed, for it could only be absorbed by complete quanta, and one quantum of energy would take the atom to a state intermediate between two of the states given by integral values of n , which is impossible. But if radiation of a frequency higher than the highest given by equation (60) (namely, that corresponding to $n=\infty$) falls on a gas it will be absorbed, for the absorption of one quantum will carry the atom beyond the state $n=\infty$, *i.e.*, it will set one electron free altogether, and endow it with a certain amount of kinetic energy in addition. This last phenomenon is simply the photo-electric effect, interpreted according to Einstein's theory; it is now seen to be a necessary logical extension of Bohr's theory of absorption.

The complete absorption spectrum ought, according to this view, to consist of a series of lines given by equation (60) and a continuous band stretching from $n=\infty$ (the head of this series of lines, given by $\nu=W_1/h$) up to $\nu=\infty$. In this spectrum the

lines would represent the reversal of Bohr's emission effect, while the band would represent the photo-electric effect.

R. W. Wood* experimenting on the absorption spectrum of sodium vapour has observed a complete absorption spectrum of exactly this type. Fifty lines were observed, agreeing exactly in position with those of the principal sodium series, and in addition a continuous absorption beginning at the head of this series and extending to the extreme ultra-violet.

* Wood, "Physical Optics" (1911), p. 513 ; Bohr, *l.c.* p. 17.

CHAPTER VI.

THE SPECIFIC HEAT OF SOLIDS.

50. According to the well-known law of Dulong and Petit, the product of the atomic weight and the specific heat of an element has, at least at ordinary temperatures, a value which is approximately the same for a great number of elements. The product is called the atomic heat, and is approximately equal to six. A simple explanation of this is provided by the usual kinetic theory of matter.

Suppose that 1 gramme of the substance in question contains N atoms, each of mass m , so that $Nm=1$. Let each atom have s degrees of freedom—that is to say, if all the other atoms are held at rest, let it be possible for each atom to have s entirely independent motions of its own. Then the expression for the energy of each atom will be that of the energy of s vibrations, and so it follows from the theorem of equipartition of energy (§ 16) that the average energy of each atom will be

$$sRT, \dots \dots \dots (61)$$

where T is the absolute temperature, and the total energy E of the substance per gramme will be $NsRT$. The specific heat will be $\frac{\partial E}{\partial T}$ in energy units, or $\frac{1}{J} \frac{\partial E}{\partial T}$ in heat units, where J is the mechanical equivalent of heat. Calling this specific heat c , we have

$$c = \frac{1}{J} \frac{\partial E}{\partial T} = \frac{1}{J} \frac{\partial}{\partial T} (NsRT) = \frac{NsR}{J} \dots \dots \dots (62)$$

Let a be the atomic weight of the element, then if m_h denotes the mass of the hydrogen molecule, the mass m of the atom now considered is $m = \frac{1}{2}am_h$. For the hydrogen molecule the value of R/m_h is known to be 4.13×10^7 , so that for the present substance $R/m = \frac{2}{a} \times 4.13 \times 10^7$, and since $Nm=1$ this is also the value of RN . The value of J is 4.18×10^7 , so that equation (62) becomes

$$c = \frac{2s}{a} \frac{4.13 \times 10^7}{4.18 \times 10^7} = \frac{1.98s}{a}.$$

The constancy of ca , which is postulated by the law of Dulong and Petit, is seen now to depend simply on the constancy of s . Moreover, s must from its meaning be an integral number, and to give to the product ac the value required by Dulong and Petit's law we must obviously have $s=3$, giving $ac=5.95$.

Each atom must have a value of s at least equal to 3, for it has three independent motions in space—namely, those parallel to the axes of x , y and z . The observed value of the product ac is thus accounted for by supposing that the atom has no further independent motions; the atoms are to be thought of as rigid points.

51. Just as in a gas, there is a distinction between specific heats at constant volume and at constant pressure, the difference between the two depending, of course, on the amount of work required to compress the heated solid back to the volume it occupied when unheated. The older experimental determinations of specific heats of solids were concerned with the specific heats at constant pressure, but recently Nernst and Lindemann* have shown how to correct such values so as to deduce the specific heat at constant volume. Now, it is to the specific heat at constant volume that the theoretical evaluation of § 50 refers. The constancy of ac ought only to be true if c represents the specific heat at constant volume.

In 1911 a series of very fine determinations of specific heats were undertaken at Berlin by Nernst and his collaborators Lindemann, Koref and others,† these determinations covering the whole range of temperature available in the laboratory. All these determinations were corrected so as to refer to specific heats at constant volume.‡

In these experiments it was found that the product ac at sufficiently high temperatures approximated very closely to its theoretically predicted value 5.95, but that there was a very remarkable falling off at low temperatures. The accompanying figure will show the general nature of the results

* "Zeitschrift für Electrochem." (1911), p. 818.

† See especially Papers by Nernst, "Annalen der Physik," 36 (1911), p. 395, and a report presented to the first Solvay congress at Brussels, 1911, "La Théorie du Rayonnement et les Quanta," p. 254. Also Papers in the "Sitzungsberichte d. Preuss. Akad.," 1911, and in the "Zeitschrift für Elektrochemie," 1911 and 1912.

‡ For the theory and details of this correction, see Nernst and Lindemann, "Zeitschrift für Elektrochem." (1911), p. 817.

obtained. The curves giving the atomic heats of four elements—lead, silver, aluminium and carbon in the form of a diamond—are shown, the atomic heat being the ordinate and the absolute temperature being the abscissa. It is found that the curves of all the elements examined show zero atomic heat at absolute zero of temperature, and tend asymptotically towards the limiting atomic heat 5.95 as the temperature increases. A still more striking discovery is that all the curves are exactly

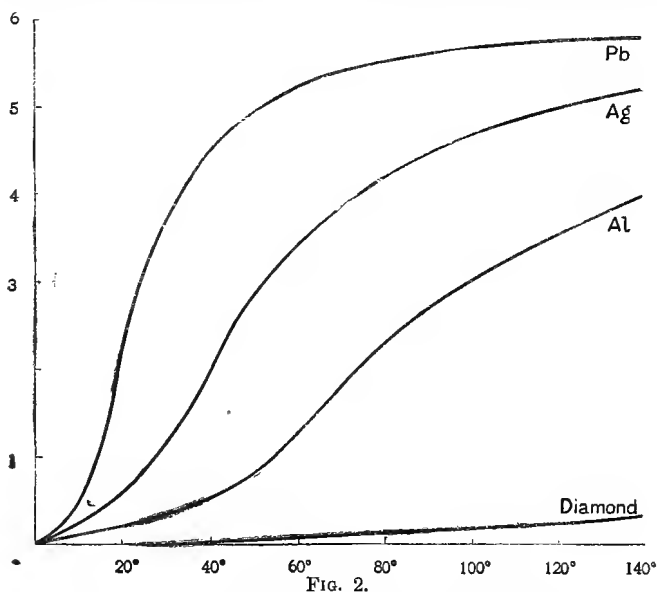


FIG. 2.

similar, except for differences in the temperature scale. Thus, if, in Fig. 2, we take the curve for silver and compress it horizontally in a certain ratio, which is about 1 : 2.3, it will be found to coincide exactly with the lead curve. Similarly, the aluminium curve, compressed in the ratio 1 : 1.8 would coincide with the silver curve, and compressed in the ratio 1 : 4.1 it would coincide with the lead curve.

52. The simple investigation of § 50 ought to apply equally at all temperatures if the fundamental principles on which it is based were sound. The principles on which the investigation was based were essentially those of the classical mechanics, so that the result of the experiments would seem to indicate that the principles of the classical mechanics are applicable

at high temperatures but not at low. This is exactly the situation which it was seen in § 31, might be expected to arise with regard to low-temperature phenomena. 'It is, therefore, natural to anticipate that the explanation of low-temperature specific heats is to be looked for in terms of the quantum-theory.

Explanations in terms of the quantum-theory, of great interest and suggestiveness, have been attempted by Einstein* and by Nernst and Lindemann.* These had, however, both a somewhat artificial element in them, and their importance lay rather in their paving the way for a final theory than in any claim to finality that they could profess. The explanation of the phenomenon, which, both from its complete naturalness and from its agreement with experiment, seems destined to be final, was given by Debye† in 1912.

53. In the analysis of § 50 we supposed each gramme of the matter under consideration to consist of N atoms, each having three degrees of freedom as though they were rigid points. There were $3N$ degrees of freedom in all, so that the total energy was, according to the older mechanics, $3NRT$, regardless of the particular nature or properties of these degrees of freedom. But according to the quantum-theory the average energy of a degree of freedom is not entirely independent of its nature; in the case of a vibration the average energy depends on the frequency of the vibration.

The atoms of the solid do not, of course, possess independent separate free vibrations. The oscillation of any one will set its neighbours into oscillation, and the free vibrations of the system are those of all the atoms simultaneously. Any motion, no matter how complicated, of the atoms can be analysed into trains of waves, just as was the case with the motion of the molecules of a gas in § 5. The number of independent vibrations of wave-length between λ and $\lambda+d\lambda$ has been seen (§ 14) to be $12\pi\lambda^{-4}d\lambda$. Of these vibrations two-thirds are waves of distortion and one-third are waves of compression. Let the former be supposed propagated with velocity V_1 and the latter with velocity V_2 , then the frequencies of the former vibrations

* The best account of these will be found in the reports of the first Solvay Congress at Brussels (1911), "La Théorie du Rayonnement et les Quanta" (1912), pp. 254, 407, in which will be found valuable discussions of the general problem. The theory of Einstein is explained later in the present report, (§ 58).

† "Zur Theorie der Spezifischen Wärmen, Annalen der Physik" 39 (1912), p. 789.

are V_1/λ and of the latter V_2/λ . It readily follows that the total number of vibrations with frequencies between ν and $\nu+d\nu$ is

$$4\pi(2V_1^{-3}+V_2^{-3})\nu^2d\nu. \quad . \quad . \quad . \quad . \quad (63)$$

There must be a limit to the values of ν possible; obviously the formula breaks down when we come to frequencies such that the wave-length is comparable with the distance between adjoining atoms. Debye assumes, as an approximation, that formula (63) is true from $\nu=0$ up to a value ν_m , which is the maximum of all the frequencies, and is determined by the condition that the total number of degrees of freedom obtained by this assumption is equal to the known total number $3N$. In other words, we must have

$$3N=4\pi(2V_1^{-3}+V_2^{-3})\int_0^{\nu_m}\nu^2d\nu=\frac{4\pi}{3}(2V_1^{-3}+V_2^{-3})\nu_m^3, \quad (64)$$

and formula (63) may be replaced by

$$9N\frac{\nu^2d\nu}{\nu_m^3}. \quad . \quad . \quad . \quad . \quad . \quad (65)$$

54. Debye proceeds by supposing that the energy of these vibrations is equal to the amount assigned to them by the quantum-theory as developed in § 18 of the present report. That is to say, each vibration of frequency ν is supposed to have an average amount of energy

$$RT \times \frac{x}{e^x-1}, \quad . \quad . \quad . \quad . \quad . \quad (66)$$

where x stands as before for $\frac{h\nu}{RT}$. Thus the total energy of the solid, obtained by integrating over vibrations of all frequencies will be

$$E=\int_0^{\nu_m} 9NRT \frac{x}{e^x-1} \frac{\nu^2d\nu}{\nu_m^3}. \quad . \quad . \quad . \quad . \quad (67)$$

Incidentally, it may be noticed that, according to the classical mechanics, we should have omitted the factor $\frac{x}{e^x-1}$ in (66), and so the total energy would have been

$$\int_0^{\nu_m} 9NRT \frac{\nu^2d\nu}{\nu_m^3} = 3NRT,$$

leading back at once to the result obtained in § 50, namely,

that the atomic heat ought to have the value 5.95 at all temperatures.

On replacing x by $h\nu/RT$, the value of E given by formula (67) reduces to

$$E = \int_0^{\nu_m} \frac{9N h \nu^3 d\nu}{\nu_m^3 (e^{h\nu/RT} - 1)} \quad \dots \quad (68)$$

The integral unfortunately cannot be evaluated in finite terms. Details of its numerical treatment and computations will be found in Debye's Paper already referred to.

55. A detailed statement of its agreement with experiment will be found in the same Paper. For the purposes of the present report the following instances will perhaps suffice.

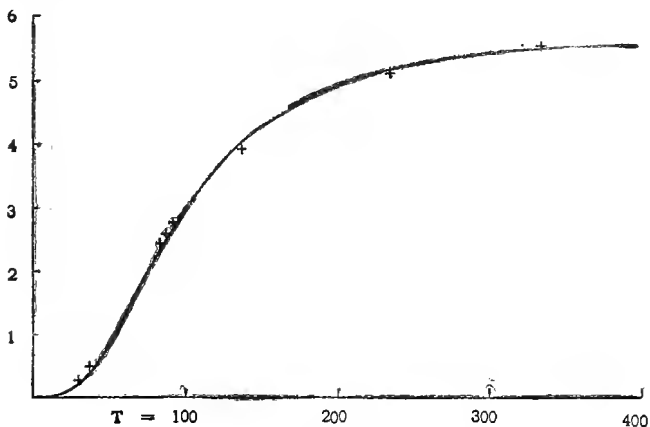


FIG. 3.

The various specific heat curves ought, as we have seen, to be dependent only on a single parameter, and this may conveniently be taken to be a quantity Θ defined by $\Theta = \frac{h\nu_m}{R}$. It is then easily seen that the specific heat at any temperature T ought to be of the form $f\left(\frac{\Theta}{T}\right)$, where f is a function of $\frac{\Theta}{T}$, which is the same for all substances. In Fig. 3, which is taken from Debye's Paper,* the continuous curve represents the graph of $f\left(\frac{\Theta}{T}\right)$ calculated from the integral (68), the scale of abscissæ

* *L.c.* p. 812.

being arranged for the value $\Theta=396^\circ$. The crosses represent the actually observed values of the specific heat for aluminium.

This figure accordingly exhibits the agreement between theory and experiment in the case of aluminium, provided that Θ , in the theoretical formula, is treated as an adjustable constant. The value of Θ for any particular substance, however, depends on ν_m , which is given by equation (64), and so admits of calculation when the elastic constants of the substance are known. The following comparison is given by Debye between observed and calculated values of Θ :—

| Element. | Θ observed. | Θ calculated. |
|----------|--------------------|----------------------|
| Al | 396 | 399 |
| Cu | 309 | 329 |
| Ag | 215 | 212 |
| Pb | 95 | 72 |

In these comparisons, the value of “ Θ observed” is obtained by fitting a curve of the type predicted by theory to the observations as closely as possible, as, for instance, has been done for aluminium in Fig. 3 above.

This will give some idea of the agreement between Debye's theory and observation. The agreement could not be expected to be perfect, for Debye's assumption of the existence of a sharply defined maximum frequency ν_m is obviously at best only a somewhat rough approximation. Various attempts have been made to improve Debye's theory in this respect; in particular, attention may be called to Papers by Born and Kármán,* in which the arrangement of atoms in the solid is treated as forming a “space-lattice” of the type with which the work of Bragg on the theory of X-ray spectra has made us familiar.† The results obtained in this way agree, perhaps, somewhat better with experiment than those obtained for the simpler theory, but it seems probable that nothing short of a complete knowledge of the structure of matter will result in any very substantial improvement on Debye's formula.

56. According to Debye's theory, the solid itself must have free vibrations of frequencies ranging from 0 to the maximum frequency ν_m . The law of distribution of these frequencies is given by formula (65), showing that the number within a given small range $d\nu$ is proportional to $\nu^2 d\nu$. Thus the spectrum of these frequencies would be a band having its head at frequency

* “Physikalische Zeitschrift,” 14 (1913), pp. 15 and 65.

† See also a Paper by H. Thirring, “Phys. Zeitsch.,” 14 (1913), p. 867, and also § 59 below.

ν_m , and falling off in intensity towards the low-frequency end. The value of ν_m can be calculated from the elastic constants of the solid by formula (64), and is found to be generally of the order of 10^{12} .

It will be noticed that this formula is derived theoretically by laying great stress on just that part of Debye's theory which is obviously most imperfect, namely, the supposition that the vibrations of the solid fall off absolutely suddenly at a certain frequency ν_m . It is, therefore, hardly to be expected that the values of ν_m calculated from it should agree exactly with the values determined from observation of the specific heat. Perhaps the most that can be expected is that the two sets of values should be approximately the same. This they may certainly be said to be, as will appear in the next section (*cf.*, table below).

57. Lindemann* has given the following formula, to some extent empirical, which is found to give the values of ν_m with surprising accuracy for the substances examined. If T_s denotes the melting point of the substance in degrees absolute, m the atomic weight and V the atomic volume, Lindemann's formula† is :—

$$\nu_m = 3.08 \times 10^{12} \times \sqrt{\frac{T_s}{mV^{\frac{1}{3}}}} \quad \dots \quad (69)$$

This agrees rather better with the observed values of ν_m than do the values calculated directly from the elastic constants, as the table below shows‡ :—

| Element. | ν_m calculated (Lindemann). | ν_m observed (spec. heats). | ν_m calculated. (elastic constants). |
|----------|------------------------------------|------------------------------------|---|
| Al | 8.3×10^{12} | 8.3×10^{12} | 8.0×10^{12} |
| Cu | 7.5×10^{12} | 6.6×10^{12} | 6.6×10^{12} |
| Zn | 4.8×10^{12} | 4.8×10^{12} | ... |
| Ag | 4.8×10^{12} | 4.5×10^{12} | 4.3×10^{12} |
| Pb | 2.0×10^{12} | 1.9×10^{12} | 1.44×10^{12} |
| Diamond | 35.0×10^{12} | 40.0×10^{12} | ... |

* "Physikalische Zeitschrift," 11 (1910), p. 609.

† In Lindemann's original Paper the multiplying constant, which is purely empirical, was taken to be 2.06×10^{12} and ν_m had a slightly different meaning.

‡ In this table the first two columns are taken from the report by Nernst in "Vorträge über die Kinetische Theorie der Materie," 1914, p. 77, and are calculated by giving the Lindemann's formula the form (69). Einstein takes the multiplying factor in Lindemann's formula to be 2.12×10^{12} , and a table of values calculated in this way is given by him in "La Théorie du Rayonnement et les Quanta," p. 415.

58. Mention must now be made of the theory by which Einstein originally attempted to explain the specific heat phenomenon. Instead of supposing the energy of the solid to reside solely in the kinetic energy of the atoms, he supposed that the atoms were absolutely at rest, and that each had three degrees of internal vibration all of the same frequency ν . On assuming that the energy of these vibrations was governed by Planck's formula (66), he arrived at the expression

$$E = 3NRT \times \frac{x}{e^x - 1} \quad . \quad . \quad . \quad . \quad . \quad (70)$$

for the total energy of the solid, as compared with the value $3NRT$ given by the classical mechanics (§ 50). On differentiation with respect to the temperature, a formula is obtained which reproduces the experimental curves of Fig. 2 in their general features, but does not agree with them to within the errors of experiment.

Einstein's explanation of specific heat must necessarily be regarded as superseded by that of Debye, but is of importance on account of the use which Nernst* has made of it in his explanation of the specific heats of compound substances. The method will be sufficiently described by considering a diatomic substance, such, for instance, as potassium chloride.

Nernst supposes the heat energy of unit mass of potassium chloride to be made up to two parts—the internal energy of the molecules, and the motion of the molecules relative to one another. The internal energy of the molecules is supposed to arise from the vibrations of the atoms relatively to one another. As a matter of geometry, there must be three degrees of freedom in these internal vibrations. Nernst supposes them all to have exactly the same frequency, and identifies this frequency with the frequency of the sharply-defined absorption band observed by Rubens in the infra-red by the method of reststrahlen.† The internal energy of the N molecules in unit mass is now given by Einstein's formula (70) in which $x = \frac{h\nu_2}{RT}$,

where ν_2 , for any substance, represents the observed frequency of the infra-red absorption band. Nernst supposes the energy of motion of the molecules as wholes to be given by Debye's

* Nernst, report in "Vorträge über die Kinetische Theorie der Materie"

† "Sitzungsber. d. Preuss. Akad. Berlin," June 5, 1913.

formula (68), the molecules now playing the part assigned to the atoms in Debye's formula. On these suppositions the total energy of the N molecules can be written down, and by differentiation the specific heat. The specific heat will be the sum of two specific heat terms, one calculated from the formula of Einstein, the other from that of Debye. If we sum these terms directly as derived from formula (68) and (70), we shall obtain twice the atomic heat, for we are now supposing that there are N molecules per unit volume.

The following specimen table, selected from several given by Nernst* in the report already referred to, will indicate the degree of closeness of agreement with observation.

Values of $2c_p$ for KCl.

| T. | Einstein term in $2c_v$. | Debye term in $2c_v$. | Correction term $2(c_p - c_v)$ | Calculated $2c_p$. | Observed $2c_p$. |
|------|------------------------------|---------------------------|-----------------------------------|------------------------|----------------------|
| 22.8 | 0.046 | 1.04 | ... | 1.086 | 1.16 |
| 26.9 | 0.13 | 1.48 | ... | 1.61 | 1.52 |
| 30.1 | 0.25 | 1.87 | ... | 2.12 | 1.96 |
| 33.7 | 0.43 | 2.25 | ... | 2.68 | 2.50 |
| 48.3 | 1.43 | 3.52 | ... | 4.95 | 5.70 |
| 57.6 | 2.13 | 4.06 | 0.02 | 6.21 | 6.12 |
| 70.0 | 2.89 | 4.57 | 0.04 | 7.50 | 7.58 |
| 86.0 | 3.66 | 4.97 | 0.06 | 8.79 | 8.72 |
| 235 | 5.55 | 5.81 | 0.32 | 11.68 | 11.78 |
| 416 | 5.83 | 5.91 | 0.68 | 12.42 | 12.72 |
| 550 | 5.87 | 5.93 | 0.90 | 12.70 | 13.18 |

The Einstein-term in the second column is calculated by assigning to ν the value actually observed for it by Rubens ($\frac{h\nu}{R}=166$); the Debye term in the third column is calculated by assigning to ν_m the value given for it by Lindemann's formula (69), and the correction term is calculated from the known physico-chemical constants of potassium-chloride. Thus the calculated values in the fifth column are in reality derived from a formula in which every constant is evaluated by experiment, and there are no adjustable constants at all. Under these circumstances the agreement between the observed and calculated values of $2c_p$ must be regarded as very remarkable, the more so in view of the fact that equally good agreement is obtained in the case of other substances for which

* *L.c.* p. 81.

ν_2 (the frequency of the rest-strahlen absorption band) is known—namely, NaCl, AgCl, KBr and PbCl₂.

Thus, it will be seen that the quantum-theory is able to predict with striking success a relation between phenomena as different in their nature as black-body radiation, the principal infra-red absorption bands of solids, and their specific heats.

An attempt has also been made by Thirring* to account for the specific heats of compounds by extending the ideas of Born and Karman† to space lattices in which two or more different masses are supposed to alternate. In this way it is found possible to calculate the relation between the elasticity and specific heat for regular crystals. The calculation is carried out for NaCl, KCl, CaF₂ and FeS₂. The author finds a mean deviation of 2.3 per cent., with a maximum of 4 per cent. from observed values through the range of temperature considered by him, a range much less than that covered by Nernst's tables.

59. There is no doubt that there must, in theory at least, be other contributions to the specific heat besides those we have been considering; what is remarkable is that the corresponding deviations from the theoretical formulæ we have had under consideration seem to be hardly noticeable experimentally. The presence of free electrons must add something to the specific heat, but it appears as though the contribution were too small to be detected experimentally. Nernst and Lindemann have found no general difference between the specific heats of good and bad conductors; Richter‡ has examined the specific heats of a series of Bi-Sn and Bi-Pb alloys with special reference to this question, and concludes that, in these alloys at all events, the free electrons do not contribute sensibly to the specific heat.

Again the rotations of the atoms or molecules must in theory contribute something to the specific heats. The atoms certainly can rotate, for if a crystal is rotated in the hand its optical axes will be found to have rotated with the body as a whole, showing that each atom must have individually changed its direction; also if a magnet is turned, its magnetic field will turn with it. The absence of a noticeable contribution to the specific heats is accounted for, on the quantum-theory, by supposing that the forces opposing rotational movements of

* "Phys. Zeitschr.," 15 (1914), p. 180, and also p. 127.

† See above, § 55.

‡ "Ann. d. Physik," 39 (1912), p. 1590.

the atoms inside the solid are so large that the corresponding vibrations are of very high frequency, and so normally possess very little energy. As far as pure theory goes, there is no question that to the terms in the specific heat contemplated by Nernst's theory (§ 58), there ought to be added an additional term, of a form exactly similar to the Einstein term, but having $x = \frac{h\nu_3}{RT}$, where ν_3 is the frequency (or average frequency) of the vibrations which depend on the rotation of the atoms.*

It is worthy of notice that sodium and mercury show an increase, beyond that accounted for by the theories we have considered, in the specific heats as the fusion-point is approached,† when presumably the intensity of the forces which prevent the atom from rotating is relaxed, and Nernst and Lindemann find that in general the same is true for the substances they have examined.

But these deviations from the simple theory are, in normal cases, too small to be detected experimentally, and it may be stated as a general rule (not applicable close to the fusion-point) that the motion of translation of the atoms suffices to account for the observed specific heats.

60. Debye's result (§§ 53, 54) may be summarised as follows :

The whole heat-energy of an element resides in the energy of its elastic-solid vibrations, the atoms being treated as the particles of the solid, and each vibration having exactly the energy allotted to it by the quantum-theory. Nernst has shown that for the compounds examined by him the same is true except that the molecules must be treated as the particles of the solid, and to the energy of the elastic vibrations of the solid must be added the energy of the internal vibrations of the molecules, each vibration again having exactly the energy allotted to it by the quantum-theory.

Both these theories, as well as the theories of Born and Karman, and of Thirring, are covered by a general explanation that the heat-energy of a solid is the energy of the vibrations of the atoms of the solid, each vibration having exactly the energy allotted to it by the quantum-theory, and therefore

* See Grüneisen, "Molekulartheorie der Festen Körper," report presented to the second Solvay Congress of Physics (Brussels, 1913) (not yet published), also A. E. Oxley, "Proc." Camb. Phil. Soc., 17 (1914), p. 450.

† Oxley, *l.c.*

having the same energy as a light vibration of identical frequency.

This recalls the result obtained in § 9, that the condition for equilibrium between a material vibration and light vibrations in the ether is the equality of mean energy of vibrations of the same frequency. This result was, in § 9, obtained from the old mechanics : the specific heat phenomenon suggests that it may be true in the quantum-mechanics also. The physical bearing of this will be discussed in the next chapter.

CHAPTER VII.

ON THE PHYSICAL BASIS FOR THE QUANTUM-THEORY.

61. The foregoing chapters have given a summary of the principal pieces of experimental evidence bearing on the quantum-theory, and a statement of some of the mathematical analysis connected with it. It has by no means been found possible to represent the quantum-theory completely by a set of mathematical equations or of physical concepts. The indications are that there is, underlying the most minute processes of nature, a system of mechanical laws different from the classical laws, expressible by equations in which probably the quantum-constant h plays a prominent part. But these general equations remain unknown, and at most all that has been discovered is the main outline of the nature of these equations when applied to isochronous vibrations.

Even if the complete set of equations were known, it might be no easy task to give a physical interpretation of them, or to imagine the mechanism from which they originate. When the equations themselves are still so incompletely known this task becomes yet harder, and so little progress has been made in this direction that an attempt to report on it reduces mainly to a chronicle of conflicting opinions.

62. The quantum-theory is believed to have disclosed in nature a certain atomicity of a kind unsuspected by the older mechanics. In the form in which the quantum-theory was originally put forward by Planck, this atomicity was in effect an atomicity of energy, although this conception was not exactly used by Planck. But the atomicity was dependent on the frequency of the energy, and seemed to have little or no meaning except in reference to absolutely monochromatic vibrations. It is more natural to suppose that the real atomicity, if it exists, is that of the entity measured by h , or by some function of h and constants of nature. The constant h is physically of the dimensions of energy multiplied by time, or action. But an attempt to imagine a universe in which action

is atomic leads the mind into a state of hopeless confusion. The classical equations can be put in the form $\delta A=0$, where A is the action and is supposed to be capable of continuous variation. If A were not supposed capable of continuous variation, but were limited to being a multiple of a unit of action, h , it might be possible to construct the true system of equations, including the quantum-theory as a special case. These equations would, of course, reduce to an expression of the principle of least action when the number of units h in the total action was very great, and so would also include the Newtonian mechanics as a special case. No progress towards the solution of this general problem has been made as yet. Mention must, however, be made of Papers by Sommerfeld,* in which a theory of an "element of action," $\frac{h}{2\pi}$ or $\frac{h}{4}$, is applied to the explanation of X-rays, γ -rays and the photo-electric effect. These serve to suggest the type of general theory which may, perhaps, be hoped for in the future, but if so, they at the same time indicate how very far the physical interpretation must be from anything at present imagined.

The quantity h or $\frac{h}{2\pi}$ is also of the same physical dimensions as angular momentum, so that if we could imagine a state of things in which angular momentum were atomic we might be in the right state of mind for attempting a physical explanation of the quantum-theory. It is to be noticed that Bohr's theory implies that the angular momentum in an atom with only one electron is always a multiple of $\frac{h}{2\pi}$, and the brilliant agreement of this part of his theory with experiment may indicate that in these cases the angular momentum of the single electron certainly behaves as though it were atomic, but this does not carry us any perceptible distance towards a physical explanation of why this atomicity exists.

The quantity hV , or $\frac{h}{2\pi}V$, is of the physical dimensions of the square of an electric charge. In point of fact, $\frac{h}{2\pi}V$, if not exactly equal, is almost equal, to $(4\pi e)^2$, i.e., to the square of the

* Sommerfeld gives an admirable summary in his report to the first Solvey Congress at Brussels (1911). "La Theorie de Rayonnement et les Quanta," p. 313.

strength of a tube of force binding two electrons. This suggests that the atomicity of h may be associated with the atomicity of e . The atomicity of e will not lead to the quantum-theory, otherwise the quantum-theory would have been fully developed long ago, but there is, perhaps, a hope that the two atomicities may be special aspects of some principle more general than either of them. It must be remembered that the atomicity of e has never received a physical explanation; it is in no way implied in the classical equations of Maxwell, and no reason is known why an electron with a charge $\frac{1}{2}e$ should not exist. Any attempt to refer back the atomicity of e to the structure of the ether simply discloses the fact that the fundamental equations of the ether are not yet fully known; it implies that if they were fully known they might be expected to contain the quantity e , and this is perhaps the same thing as saying that they would contain the quantity h . It may be that if the equations of the ether were fully known they would be seen to involve the quantum-theory. If $\frac{h}{2\pi}V$ is the same

thing as $(4\pi e)^2$, an attempt to give a physical explanation of the quantum-theory might be based on the atomicity and possible discrete existence of tubes of force of strength $4\pi e$, ideas with which we have been made familiar in the writings of Sir J. J. Thomson.* These ideas seem to many physicists to be at variance with experience, but they have to their credit that they give a natural and simple explanation of the electrokinetic momentum in the ether,† such as I believe cannot be given by any other series of physical conceptions.

63. It may, perhaps, be accepted that it is yet too early to expect an explanation, in anything like fundamental terms, of the meaning of the quantum-theory, and we may attempt merely to understand some of the physical processes implied in the established results of this theory. Even as regards this preliminary problem there is no general agreement.

Physically, the quantum-theory undoubtedly centres round the idea of spasmodic or instantaneous interchanges, losses or gains of energy of amount $\varepsilon = h\nu$. This idea involves the conception of two receptacles of energy, but the quantum-theory gives no indication as to what these receptacles are, or when or why they lose or acquire energy.

* "Recent Researches in Electricity and Magnetism" (1892), Chapter I. and later books.

† "Elements of Electricity and Magnetism," 3rd Edition (1904), p. 279.

In Planck's original theory,* it was supposed that all matter contained large numbers of resonators of different frequencies ; these were capable only of holding energy in quanta, and the spasmodic interchanges of energy took place between different resonators. The theory was open to somewhat obvious objections which have been repeatedly urged against it. In the first place an interchange of energy between resonators of the same frequency does nothing to advance the progress towards the final steady state, while interchanges of energy between resonators of different frequencies are in general impossible owing to the incommensurability of the quanta corresponding to different frequencies. This difficulty might be met by supposing that there is some other receptacle for energy, in which the energy is not limited to existence only in complete quanta as, for instance, the ether or possibly free electrons. This conception, however, is not part of Planck's original theory, and is certainly open to many objections.

The specific heat formula of Debye implies that in a solid there are no receptacles of energy except the elastic-solid vibrations of the matter, and the ether. It would (*cf.* § 59) be straining the evidence to conclude that there is no possibility of any further receptacles of energy in matter, but it is significant that Planck's assumed resonators have given no direct indication of their existence. Resonators of infinitely varied frequencies, as assumed by Planck, would imply an infinite variety of atoms or molecules in the solid unless they are of such a scale as to involve relations between different atoms or molecules, in which case they merge into the elastic-solid vibrations of Debye. Resonators of a few definite frequencies are not what is required by Planck's theory, and their existence seems to be put out of question from their not proclaiming themselves spectroscopically.

Perhaps Planck's original theory seems best capable of coming into line with the known facts of physics if his resonators are definitely identified with the elastic vibrations of the solid. This identification removes one objection which has frequently been brought against Planck's theory. The first part of his proof consists in showing that in equilibrium the mean energy of a resonator must be equal to the mean energy of an ether-vibration of the same frequency. Planck bases this proof on the classical mechanics ; in fact, his proof is in

* " *Annalen der Physik*," 4 (1901), p. 553

essence the same as that given in § 9 of the present report. Now, it is easy to point out that it is inconsistent to assume, as Planck does in the first part of his theory, that the energy of the resonators can change continuously according to the classical laws, and afterwards to assume that the energy can only change by complete quanta. If, however, the resonators are interpreted simply as the elastic-vibrations of the solid then the equality of the mean energies in matter and ether may be treated as an experimental fact; the supposition that the energies are equal is the basis of Debye's theory of specific heat, and is fully confirmed by observation. The fact that these energies are equal is perhaps (if the classical dynamics are no longer valid) a fact which still demands explanation, but there is no question that it is a true fact. But even if the resonators are identified with the elastic-vibrations, we are no nearer to discovering a mechanism which will make it possible for the energies to change only by complete quanta—indeed, the proposed identification makes any such hope seem infinitely remote. And it must also be noticed that the frequencies of the “resonators” provided by Debye's elastic-solid vibrations are limited to the infra-red end of the spectrum, whereas Planck's theory demands resonators of frequencies ranging through the whole spectrum.

In the later forms assumed by Planck's theory it is supposed that the resonators emit their radiation in complete quanta, but that they absorb it in a continuous manner. Thus the energy of a resonator at any instant may be anything: it is not restricted to being an exact multiple of a quantum. This idea is attractive physically, for it minimises the divergence from the older electromagnetic theory, and is capable of reconciliation with the undulating theory of light, but it is questionable whether it is really consistent with the quantum-theory itself. If the energy of a resonator can vary continuously, we must not deduce the radiation-formula from the supposition that it must be an integral multiple of a quantum; and Poincaré's analysis (§ 23) seems to indicate that Planck's radiation formula can only be true if the energy of the radiation *cannot* vary continuously.

It may be remarked that Planck's physical theories deal only with one special mechanism of radiation, whereas the considerations mentioned in § 8 of the present report indicate that there must be many mechanisms, and that each one independently must lead to Planck's formula. Thus the

physical problem apparently cannot be solved by attributing special properties to Planck's radiators; what is ultimately needed is a new system of mechanics which will endow all radiators with these properties.

That this new mechanics must be of a very comprehensive nature becomes evident on considering the result obtained in § 10 of the present report. It was there seen that free electrons and ether, interacting according to the classical dynamics, would set up Lord Rayleigh's law of radiation. It is, therefore, evident that the interaction between the ether and free electrons cannot be governed by the classical mechanics: the new mechanics must differ from the old even as regards the motion of free electrons.

For this reason it seems useless to attempt to explain away the conflict between the radiation-laws and the classical mechanics by ingeniously devised special models of atoms, or special detailed mechanisms of emission of radiation, which might seem, while obeying the classical laws, to give something approximating to Planck's law. Any such attempt would first have to surmount the difficulty that any system whatever, if it obeys the classical laws, must also in its state of thermodynamical equilibrium obey the law of equipartition of energy, which is known in turn to lead to Rayleigh's radiation formula (§ 17). And if this difficulty could be turned, as, for instance, by postulating a final state which was not one of thermodynamical equilibrium, the question of why all possible mechanisms of radiation lead to Planck's law, as they certainly appear to do (§ 8) would remain untouched. And finally, if single electrons do not obey the classical laws, there would seem to be little gain in proving, if it could be proved, that complicated structures might possibly obey them.

64. The mechanism of the emission of radiation such as figures in the line-spectrum of a gas is very clearly pictured by Bohr's theory, and the marked agreement of this theory with observation certainly raises a strong presumption that his premisses contain at least some truth. It is difficult to see how his final equations could stand at all unless it is assumed that the emission of radiation is in complete quanta, and is an emission of monochromatic light. Absolutely instantaneous emission is not in any way required, but the emission must be catastrophic in the sense that when once it has started nothing can stop it until a whole quantum has been set free.

Again the whole evidence of the photo-electric effect is that,

in this phenomenon at least, the absorption must be in complete quanta, and moreover that the energy of each quantum must be in such a concentrated form that it can all be absorbed by one atom.

The whole of the phenomena associated with the quantum-hypothesis could probably be given a consistent physical explanation if we were free to imagine radiation to be atomic in its structure, consisting of indivisible quanta of radiation, each monochromatic and highly concentrated in space. The quanta might, perhaps, almost be thought of as corpuscles of radiation, travelling through space with the velocity of light, emitted and absorbed as complete entities, and entirely incapable of any kind of sub-division. Ideas of this kind constitute Einstein's theory (*see above*, §44) of "light-quanta."

Somewhat similar ideas had been formulated before the rise of the quantum-theory, in particular by Sir J. J. Thomson,* who regarded the Faraday tubes as having discrete existence in the ether. This train of ideas is discussed by Whetham† as follows :—

"Faraday's tubes, it is clear, give a very powerful and convenient method of studying the phenomena of the electromagnetic field, and indications are not wanting that they represent something more than a useful mathematical fiction. If the structure of the electric field be discontinuous in reality, as our tube-picture or it indicates ; if the electric and magnetic effects of a charge of electricity are in reality exerted throughout the surrounding space by means of discrete tubes of force-vortex filaments in the ether, or whatever they may actually be, an advancing wave of light must be discontinuous also. Could we look at such a wave from the front and magnify it millions of times we should see not a uniform field of illumination but a number of bright specks scattered over a dark ground. Each tube of force would convey its own tremors, and these would constitute light, but between them would lie undisturbed seas of ether.

"Such an idea about the nature of a wave-front of light is very unexpected and surprising. We are inclined at once to relegate our tubes of force to a museum of conceptional curiosities. But it is a remarkable thing that certain evidence in favour of the discontinuous nature of a wave-front really does exist."

* *See*, in particular, Camb. Phil. Soc. "Proc.," 14 (1907), p. 417.

† "Experimental Electricity" (1905), p. 207.

The evidence referred to arose from a study of the ionisation of gases by X-rays. It was noticed that the ionisation was such as would be expected if the X-rays did not spread out in accordance with the undulatory theory of light, but moved with their energy concentrated as described.* It is now believed that the ionisation produced by the X-rays is produced by the intermediary agency of β -rays, and this somewhat alters the problem. The question now becomes how the X-rays, if they are not concentrated, can produce β -rays as they do, and the problem really becomes similar to that of the photo-electric effect, discussed in § 48 of the present report. In any case the phenomena of the production of β -rays by X-rays and the emission of electrons by ultra-violet light both suggest very strongly the possibility of radiation being propagated in the form of concentrated "atoms" or quanta.

65. This view, however, has been unable to gain acceptance owing to its obvious conflict with the well-established principles of the undulatory theory of light. For instance, Prof. Lorentz says :—†

"Now it must, I think, be taken for granted that the quanta can have no individual and permanent existence in the ether, that they cannot be regarded as accumulations of energy in certain minute spaces flying about with the speed of light. This would be in contradiction with many well-known phenomena of interference and diffraction. It is clear that, if a beam of light consisted of separate quanta, which, of course, ought to be considered as mutually independent and unconnected, the bright and dark fringes to which it gives rise could never be sharper than those that would be produced by a single quantum. Hence, if by the use of a source of approximately monochromatic light, we succeed in obtaining distinct interference bands with a difference of phase of a great many, say some millions, of wave-lengths, we may conclude that each quantum contains a regular succession of as many waves, and that it extends therefore over a quite appreciable length in the direction of propagation. Similarly, the superiority of a telescope with wide aperture over a smaller instrument, in so far as it consists in a greater sharpness of the image, can only

* See Campbell, "Modern Electrical Theory," 1st Edition (1907), p. 226.

† Discussion on "Radiation" at the Birmingham Meeting of the British Association (1913). See also a short article, also by Lorentz, "Die Hypothese der Lichtquanten," "Phys. Zeitsch.," 11 (1910), p. 349.

be understood if each individual quantum can fill the whole object-glass.

"These considerations show that a quantum ought at all events to have a size that cannot be called very small. It may be added that, according to Maxwell's equations of the electromagnetic field, an initial disturbance of equilibrium must always be propagated over a continually increasing space."

Certainly every one of the objections stated in this short paragraph seems to be insuperable. It may be added that the question of the indivisible existence of quanta in the ether has been tested directly, or as directly as is possible, by experiment.

If light occurred only in quanta, interference could only occur at a point at which two or more quanta existed simultaneously. If the light were sufficiently feeble the simultaneous occurrence of two quanta at any point ought to be a very rare occurrence, so that all phenomena, such as diffraction patterns, which depend on interference, ought to disappear as the quantity of light present is reduced. Taylor* has shown that this is not the case; he reduced the intensity of his light to such an extent that an exposure of 2,000 hours was necessary to obtain a photograph, and yet obtained photographs of diffraction patterns in which the alternation of light and dark appeared with undiminished sharpness. In Taylor's experiments the intensity of light was 10^{-16} ergs per cubic centimetre, or about one light-quantum per 10,000 cubic cm., so that if the quanta had been concentrated nothing of the nature of a diffraction pattern could possibly have been observed.

Thus it appears that there is no hope of reconciling the undulatory theory of light with the quantum-theory by regarding the undulatory-theory as being, so to speak, only statistically true when a great number of quanta are present. One theory cannot be the limit of the other in the sense in which the Newtonian mechanics is the limit of the quantum-mechanics, and we are faced with the problem of combining two apparently quite irreconcilable theories.

66. A question intimately involved in any attempt to find a physical basis for the quantum-theory, is that of the degree of reality or substantiality with which the ether must be supposed endowed. The modern school of British physicists have been inclined to regard the ether as a completely real substance—indeed to some of them the ether is the primary real substance

* "Proc. Camb. Phil. Soc.," XV. (1909), p. 114.

of the universe. At the other extreme stands the relativity school, who almost deny that the ether has any reality at all. There are innumerable intermediate positions between these two extremes.

For the physical interpretation of the quantum-theory the precise question which is of importance is whether the ether has so much of substantiality that it must be treated as part of the dynamical system in connection with which it occurs. To the relativity school, to speak of the "dynamics of the ether" would be as meaningless as to speak of the "dynamics of space."

If the ether is part of the dynamical system, then the energy in the ether must be treated as part of the energy of the system, and the waves or vibrations which are possible in the ether will represent just so many additional degrees of freedom of the whole system. The final state of this system can be treated as a problem in statistical mechanics, and to arrive at Planck's formula it would appear (cf. § 26) to be necessary to suppose that the vibrations in the ether themselves gain or lose energy by whole quanta. This is, of course, in accordance with the suppositions of Bohr's theory, and with the evidence of the photo-electric effect. It is worth noticing that this in itself does not imply any departure from Maxwell's equations *for free ether*, because these equations are not concerned with the interchange of energy between vibrations of different wave-lengths in the ether. Such an interchange requires the presence of matter in some form or other, and an interchange by quanta would require only a modification of the classical equations for the case in which ether and matter are present together. On the other hand, the photo-electric effect seems to demand a concentration in space of the energy of the quanta, and this certainly does demand a modification of Maxwell's equations even for free ether. For Maxwell's equations indicate that the energy ought to spread out in all directions in space, and under these equations no quantum could remain in a concentrated form.

67. If the ether is regarded as too devoid of substantiality, to be treated as part of the dynamical system, it is necessary to fall back on to the changes of energy in the mechanism by which the radiation is produced. Almost all the Continental physicists have regarded the quantum-theory from this point of view, which has the disadvantage that it is necessary to specify exactly the mechanism of radiation. Whatever this

mechanism may be, and however many types of mechanism there may be, it is necessary that the energy of each should jump by quanta. So far no success has attended any explanation of why the energy of any type of mechanism should be incapable of changing except by quanta: assuming the fact, of course, the required results following, but the difficulty lies in making the assumption of the fact seem physically plausible.

68 Whatever rôle is assigned to the ether, the main physical difficulty about the quantum-theory at present seems to be the apparent impossibility of reconciling it with the established results of the undulatory theory of light. The experimental evidence—for instance, of the photo-electric effect and of interference—seems almost to indicate that both theories are true simultaneously: that radiant energy both remains concentrated and indivisible, and at the same time spreads and is divisible: the idea that these two phenomena may be concerned with two totally different kinds of radiation seems at present too fantastic for serious consideration. In any case it may be asserted with confidence that until some kind of reconciliation can be effected between the demands of the quantum-theory and those of the undulatory theory of light, the physical interpretation of the quantum-theory is likely to remain in a very unsatisfactory state. Probably the hope of most physicists is that some sort of a compromise may ultimately be effected, but at present any practical attempt at a compromise appears to require the abandonment of something which is essential to one or other of the two theories. And it must be remembered that any hope of a compromise is to a very large extent excluded by Poincaré's arguments, already summarised in § 27 of the present report: the explanation of the black-body spectrum demands the quantum-theory and nothing but the quantum-theory, all the discontinuities of the theory and their surprising physical consequences included. The keynote of the old mechanics was continuity, *natura non facit saltus*. The keynote of the new mechanics is discontinuity; in Poincaré's words:—

“Un système physique n'est susceptible que d'un nombre fini d'états distincts; il saute d'un de ces états à l'autre sans passer par une série continue d'états intermédiaires.”

The antithesis is obvious; its resolution will not be easy. Perhaps the present report cannot end better than by a free

translation of Poincaré's concluding remarks in his striking article, "L'hypothèse des Quanta":—*

"We see now how this question stands. The old theories which seemed until recently able to account for all known phenomena have suddenly met with an unexpected check. Some modification has been seen to be necessary. A hypothesis has been suggested by M. Planck, but so strange a hypothesis that every possible means was sought for escaping it. The search has revealed no escape so far, although the new theory bristles with difficulties, many of which are real and not simple illusions caused by the inertia of our minds, which resent change.

"It is impossible at present to predict the final issue. Will some entirely different solution be found? Or will the advocates of the new theory succeed in removing the obstacles which prevent us accepting it without reserve? Is discontinuity destined to reign over the physical universe, and will its triumph be final? Or will it finally be recognised that this discontinuity is only apparent, and a disguise for a series of continuous processes. The first observer of a collision thought he was witnessing a discontinuous process, but we know to-day that what he saw was the result of changes which, although very rapid, were continuous. Any attempt at present to give a judgment on these questions would be a waste of paper and ink."

* "Dernières pensées," H. Poincaré (Flammarion, Paris. 1913)

